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## Abstract

Water quality data spanning 13 years and covering an extensive range of major, minor and trace elements in rain and stream waters at Plynlimon in mid Wales, are presented. Rainfall water chemistry is highly variable due to varying proportions of marine and pollutant derived constituents associated with patterns of atmospheric circulation. Stream waters, being composed of different proportions of waters from three chemically distinct sources at any one time (atmospheric deposition, the soil system and deeper groundwaters), are also chemically highly variable. For example, components predominantly derived from deposition such as chloride change only in response to sea-salt deposition episodes. Solutes associated with bedrock weathering such as calcium, magnesium, and alkalinity decrease with increasing flow, those associated with the upper soil layers such as aluminium, many transition metals, dissolved organic carbon and hydrogen ions increase with increasing flow. The nutrients (e.g. nitrate, boron, bromide and iodine) exhibit strong seasonal cycles associated with cycles of vegetation growth and decay.

The changes in stream water chemistry resulting from tree harvesting in the Afon Hore catchment are shown to have run their course within a period of eight years. Nutrient increases in the first few years following the commencement of felling have returned to or fallen below pre-felling values. Aluminium changes are shown to be complicated by changes in nitrate and calcium. Aluminium concentrations initially increased and have fallen below their pre-felling value. Data for chloride suggest a reduction in capture of dry and mist deposition; this indicates the importance of understanding reduced deposition as a result of felling. Felling has also affected the soil micro-climate which experiences greater fluctuations in temperature and an increase in the concentration of constituents associated with organic matter.

Input-output mass balance estimates show that atmospheric inputs of many constituents are retained strongly by the catchment (e.g. ammonium, phosphate, barium, boron, lead and iodine). In contrast, many of the transition elements as well as divalent base cations, aluminium and alkalinity show a net release from the catchment. Conservative constituents such as chloride and sodium show a net input-output balance.

## Introduction

In the spring of 1983, a research programme was initiated into the hydrogeochemistry of an upland UK environment (Neal, 1990a); its aims were to characterise the effects of atmospheric pollution by acidic oxides and forestry management on stream water quality, as these are major UK environmental issues for the uplands (Stonor and Gee, 1985; Edmunds and Kinniburgh, 1986; Neal *et al.*, 1986, 1992a,b; UKAWRG, 1988; Reynolds *et al.*, 1988, 1989; Nisbet, 1990). Two main sub-catchments of the headwaters of the River Severn in the Hafren forest, Plynlimon, mid-Wales, were chosen for study. Because a major deforestation programme was planned for one of the two sub-catchments, and detailed hydrological data for both these catchments are available; they comprise an integral part of the Institute of Hydrology's water balance studies at Plynlimon (Newson, 1976; Kirkby *et al.*, 1991). From its inception, the underlying approach of the hydrochemical study was to examine the behaviour of a wide range of chemical constituents. The reasons for this were two-fold. Firstly, it was essential to assess hydrological flow pathways at the catchment level. To this end, it was decided to apply chemical fingerprinting techniques using components with very different chemical properties. The idea, analogous to that used for the development of the periodic table, was to investigate the possibility that associations of behaviour for the chemical constituents might provide an insight into the underlying hydrogeochemical functioning of the environment (Neal and Rosier, 1990; Neal *et al.*, 1988a,b, 1990b,c, 1997a,b,c; Robson and Neal, 1991; Neal and Hill, 1994). Secondly, environmental issues concerning the influence of man on the upland environment were being addressed; analyses for a wide range of chemical elements was essential—how could such environmental

impacts be assessed without a knowledge of the components that were changing under man's influence; and such changes might also be detrimental to the acidic and acid sensitive UK upland environment (Neal *et al.*, 1992a,b)?

This paper summarises the water quality of atmospheric deposition and of stream waters draining these catchments, thus providing a hydrochemical compendium of one of the most extensive and detailed studies undertaken at a UK upland site. An analysis of long term inputs, of the impacts of conifer harvesting and replanting and of input-output budgets is made, indicating the major hydrochemical processes occurring within a period of varying pollutant deposition. This information on a UK acid sensitive upland system subject to acidic deposition and land use change is of value from both a scientific and environmental management stand-point at both the catchment and regional level.

## Description of the Study Area

The work relates to two streams, the Afon Hafren and the Afon Hore, which form the main head water drainage of the River Severn in mid-Wales. Bedrock geology consists of lower Palaeozoic mudstones, greywackes, sandstones and grits. The overlying soils are thin (typically 70 cm); stagno-podzols predominate in a mosaic of acid upland types including peats, brown earths and stagno-gleys. A typical soil profile has organic-rich 'L' and 'O' horizons (3 to 10 cm); the lower soils consist of a leached 'E' horizon (10 to 20 cm) and a fine textured podzolic 'B' horizon (about 40 cm thick) merging into a mineral 'C' horizon (see Reynolds *et al.*, 1988). Vegetation cover on the tops of the catchments is dominated by acid grassland. On the lower parts of the two sub-catchments on acid moorland, plantation forestry (predominantly Sitka spruce, *Picea sitchensis*) was introduced in various phases between 1937 and 1964.

Apart from minor 'thinning' of the forest stand, harvesting did not begin until late spring 1985 when clear felling of the lower half of the Afon Hore commenced. This felling took 3 years to complete. In the process, extensive brash and tree stumps were left to decompose in situ. Soon after harvesting, replanting of the slopes with juvenile Sitka spruce (<1 m high) proceeded.

Rainfall averages about 2500 mm $yr^{-1}$ with evapotranspiration loss typically amounting to 500 and 650 mm $yr^{-1}$ for the Afon Hafren and Afon Hore respectively. Being next to each other, of similar altitude range and similar size (Table 1), the streamflow responses to storm events are similar and in phase for the two sub-catchments. The hydrograph response to storms is both rapid and 'flashy'; flows vary between 0.01 and 4.5 $m^3$ $s^{-1}$ (Newson, 1976; Kirkby *et al.*, 1991).

Rainfall chemistry is represented by a weekly composite sample from two open collectors near the top and the bottom of the altitude range spanned by the catchments; sampling began in May 1983. A weekly grab sample is taken from the lower stretches of the Afon Hafren and Afon Hore. Initially, the Afon Hafren stream was monitored to provide a control against which to compare the hydrochemical impacts of tree-felling on the Afon Hore. Unexpectedly, important hydrochemical differences were found between the two streams; these were due to small differences in the degree of calcium carbonate mineralisation in the bedrock of the two sub-catchments (Reynolds *et al.*, 1986; Neal *et al.*, 1990a). The Afon Hore has higher pH (typically by 0.5 pH units) and higher base cation concentrations (a factor of about 4). For this reason, the Afon Hafren was inappropriate as a control and a second alternative control site on the Afon Hore, above the harvested area, was chosen. This 'upper' Hore site is about half way between the top of the catchment and the lower Afon Hore monitoring point; about 50% of the catchment was afforested (Table 1). Monitoring of this extra site began in September 1984. Since that time several other sites have been established. However, the examination presented here concentrates on the sites mentioned above plus a cloud-water monitoring site on the upper plateau region of the Severn catchments established in 1991. The cloud-water collector is of the passive, lidded 'harp type' described by Milne *et al.* (1988) and Reynolds (1991). In brief, the collector consists of a low density polyethylene-coated metal frame over which an inverted cone of nylon filaments is stretched. Beneath the collector, a 30 cm diameter glass funnel directs the moisture droplets into a polypropylene bottle. The whole assembly is capped with a 1.2 m diameter lid mounted on a tubular steel framework to exclude droplets of greater than 5 mm diameter at wind speeds of up to 5 m $s^{-1}$. Some rainwater contamination can occur under windy conditions, but the collectors provide good qualitative estimates of cloudwater chemistry (Crossley *et al.*, 1992).

Two sub-samples of each of the original samples of the different water types collected were taken for analysis in the IH laboratories. One sub-sample was filtered with 0.45 $\mu$m membranes and acidified with high purity concentrated nitric acid to 1% v/v within 2 hours of sampling. This sub-sample was then stored in the dark at 4°C in 10% acid-washed polyethylene bottles prior to analysis.

*Table 1.* Catchment details of streams sampled: * indicates catchment fully felled during the sampling period.

| Catchment | Area (ha) | Altitude range (m) | % forest | % peat and moorland |
|---|---|---|---|---|
| Afon Hafren | 347 | 350–690 | 52 | 48 |
| Upper Hore | 178 | 405–738 | 56 | 44 |
| Afon Hore* | 335 | 339–738 | 78 | 22 |

The acidification minimized the loss of metals through adsorption to the bottles and precipitation reactions.

Analysis of the acidified sub-sample was as follows; inductively-coupled-plasma optical emission spectrometry (ICPOES) for Ca, Mg, Na, $SO_4$, Mn, Fe and atomic absorption spectrophotometry (AA) for K. From May 1983 to January 1988, ICPOES analysis was made on twenty-fold preconcentrated samples for the trace metals, transition elements, lanthanides (La, Ce and Pr) and actinides (Th and U). From January 1988 to November 1992 both ICPOES and inductively-coupled-plasma mass spectrometry (ICPMS) analyses were undertaken. This changeover reduced analytical times significantly; the ICPMS did not require a preconcentration step due to its much greater analytical sensitivity. The overlap period ensured a rigorous test for the reproducibility of the method and excellent results were obtained. From November 1992 onwards, after this 'proving' time, only the ICPMS analysis was performed. With each batch of samples for ICPOES and ICPMS analysis, the Institute of Hydrology's own quality control standards were included. International quality control references were also analyzed and cross checked against the Institute of Hydrology's quality control standards once a week. The second sub-sample was filtered with 2 $\mu$m glass fibre filters into chromic acid-washed glass bottles and stored with the other sub-samples prior to analysis. These sub-samples were analysed colorimetrically for F, Cl, Br, I, $NO_3$, $NH_4$, $PO_4$ and Si. Dissolved organic carbon (DOC) was analysed using a TOCsin II aqueous carbon analyser.

Electrical Conductivity (EC), and pH were determined by electrometric techniques and Alkalinity ($Alk_{Gran}$) by Gran titration on unfiltered samples at field temperature at the Plynlimon field station. For the measurement of pH, samples, electrodes and buffer solutions were maintained close to field temperature to minimise error due to drift and to provide conditions representative of the field situation. Quality control checks were also undertaken using a standard 0.0001N sulphuric acid standard (pH 4.01±0.02). $Alk_{Gran}$ was determined electrometrically using an acidimetric titration over the pH range 4.5 to 4.0 throughout the period: the analytical protocols and methodology are provided by Neal *et al.* (1988a) and Robson (1993). In recent years, $Alk_{Gran}$ has also been determined in the pH range 4 to 3 to account more fully for the influence of organic acid on the total alkalinity. As the two measures of Gran alkalinity were found to be very similar, only the data for titration from pH 4.5 to 4.0, are presented in this paper as this measurement provided the longer and more complete record.

## Results and Interpretation

To summarise the Plynlimon data set on water quality is a daunting task given the length of record and breadth of information to be represented. In this paper, a two fold approach has been taken. Firstly, the reader is provided with tabulated summary statistics and time-series plots of the raw data (Appendix Tables 1 to 5 and Appendix Figure 1). Secondly, general features of the atmospheric inputs and the streamwater chemistry of undisturbed forested and harvested catchments are pulled-out and illustrated in the main text. Input-output budgets are then presented and the results are integrated in the summary section.

### ATMOSPHERIC INPUTS

Deposition chemistry at Plynlimon is influenced heavily by the maritime climate experienced in the UK and is characterised by two specific groups of constituents; those of marine origin (sodium, magnesium, strontium, bromide, chloride, calcium, sulphate and potassium) and those of terrestrial or anthropogenic pollutant origin (nitrate, non-marine sulphur, ammonium, DOC and metals such as lead, zinc, chromium, aluminium, cadmium and iron). The supply of marine or terrestrial components is dependent on weather patterns. Plynlimon is close to the Irish sea and the North Atlantic Ocean and strong westerly and south-westerly winds provide rainfall enriched in the marine constituents; light easterly winds bring air with high levels of terrestrial/anthropogenic contaminants.

The concentrations of both marine and terrestrial components are very variable (Appendix Table 1, Appendix Figure 1). The marine components are transferred from the sea to the atmosphere as sea-spray (Cryer, 1986), and their ratios remain close to those of sea-water. Both concentrations and loads of sea-salts deposited on the Plynlimon catchments show marked seasonality. Their values peak in the autumn and winter, coinciding with high rainfall volumes associated with the progression of low pressure systems from the Atlantic. The annual variations in catchment loadings of Ca, $SO_4$ and K are complicated by the dual sources of these constituents. Sulphate loads at Plynlimon correlate with south-westerly and westerly winds, the highest rainfall volumes also coincide with these wind directions resulting in high sulphur loadings from marine sources, whereas the highest sulphur concentrations in rainfall are non-marine in origin.

In contrast to the marine constituents, light easterly winds associated with high pressure systems in the spring/summer bring air that has passed over agricultural land and industrial areas resulting in high concentrations of non-marine sulphate, nitrate and ammonium, as well as hydrogen ion concentration and metals. Concentrations increase with decreasing volume of catch for most of the pollutant components in line with pollutant wash out mechanisms in the atmosphere. However, there is no corresponding systematic concentration variation for the marine components (e.g. Na, Cl, Mg, Br: Appendix Table 1).

While there is high data scatter, there are longer term patterns in inputs for sea-salts, chromium lead, and zinc

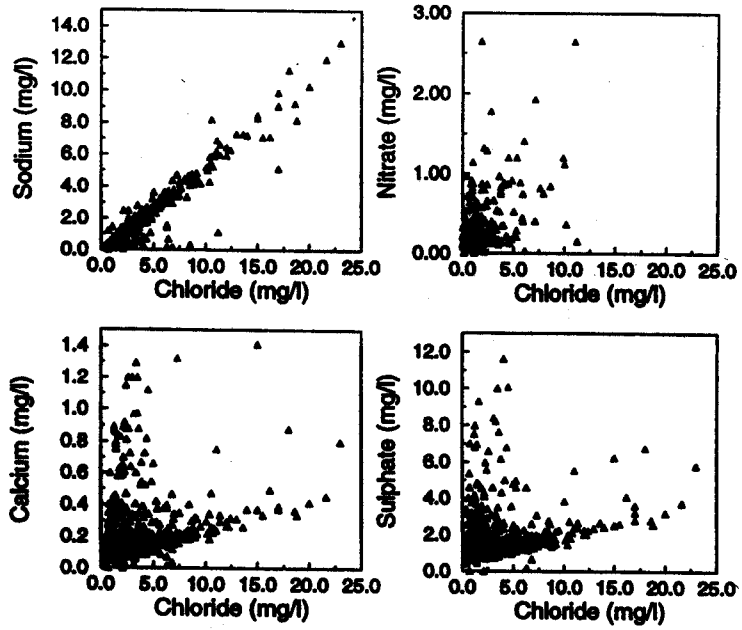


Fig. 1. *Plots of concentrations of sodium, calcium, sulphate and nitrate against chloride for rainfall.*

but there is no general trend with time (Figure 2 and 3: Appendix Figure 1: see also Wilkinson and Jenkins, 1996 and Robson and Neal, 1996). For zinc, the higher concentrations occur for years of relatively low sea-salt inputs and this probably reflects the relative importance of Atlantic frontal systems and complex air masses that have travelled over the industrial centres of Wales and England. In the case of lead, it seems that there has been a major increase in concentration in rainfall over the past few years (Neal *et al.*, 1996).

In mist, concentrations of most determinands are high compared to rainfall and there remains a similar subdivision between marine and pollutant components (Appendix Table 2; see also Wilkinson *et al.*, this volume). In general,

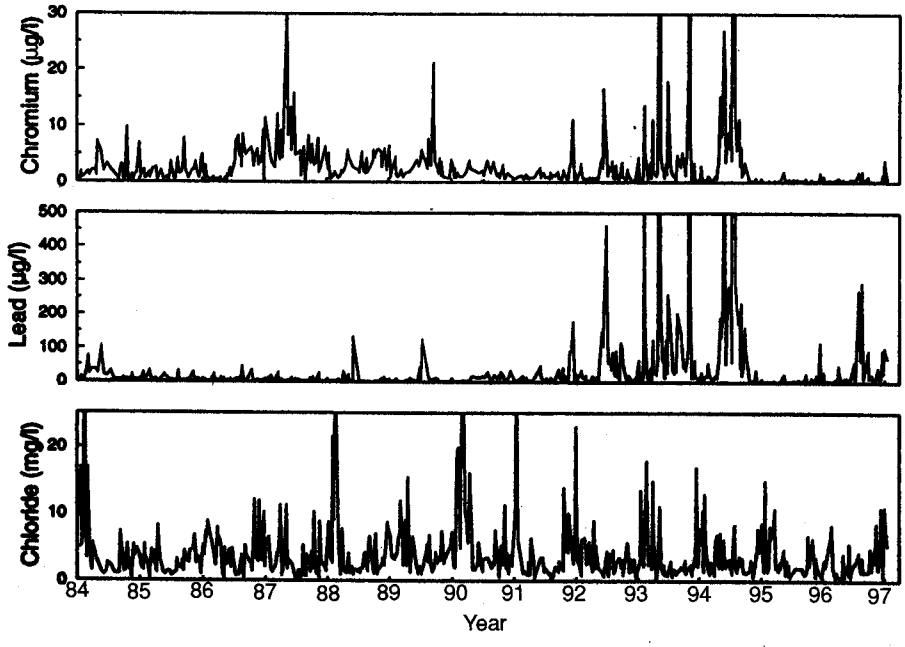


Fig. 2. *Time series plots of chloride, chromium and lead in rainfall.*

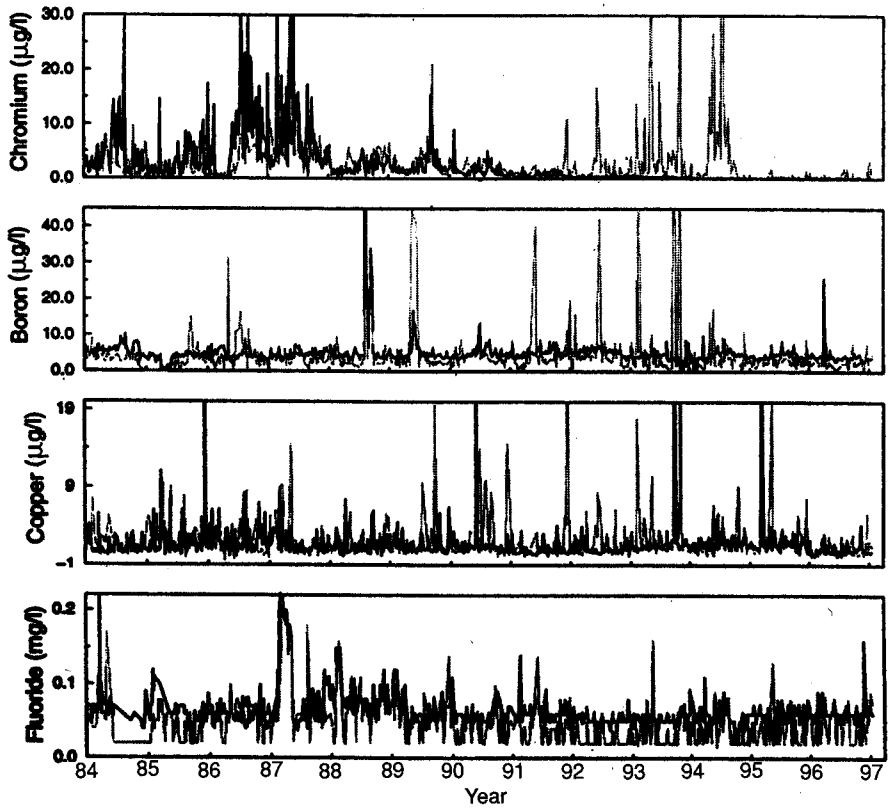


Fig. 3. *Time series plots of zinc, chromium and fluoride concentrations in rainfall (feint line) and Afon Hafren water (dark line).*

concentrations decrease with increasing volume of catch and this applies to both the marine and pollutant components. Mist and dry deposition provides an important source of chemicals to the catchment. For example, about 40% of the sea salts and 35% of the sulphate come from sources other than wet deposition on the forested catchments at Plynlimon. For the moorland areas, these values are around 15% and 10%, respectively (Wilkinson *et al.*, 1997). In terms of the pollutant inputs of sulphate, nitrate and ammonium as wet deposition alone, their concentrations are relatively low for the UK, although the high annual rainfall volume means that the fluxes entering the catchments are relatively high (Table 2). Total trace metal deposition on both moorland and forested areas of Plynlimon (Wilkinson *et al.*, 1997) are low compared with many areas of the UK (Cawse, 1981). This is due to the lack of heavy industry in mid-Wales; the predominance of marine inputs from the south-west result in high loadings of the marine components compared to other UK sites.

## RUN-OFF CHEMISTRY OF FORESTED AREAS

For all but a few constituents of the stream waters draining the Plynlimon catchments, the concentrations observed are controlled by within-catchment sources and processes. The relative contributions of these different sources vary with flow, with the seasons and at longer time scales associated with, for example, droughts. Appendix Tables 3 to 5 summarise data for the three monitored locations discussed in this paper. The base and storm flow values are the mean of the concentrations in the lowest and highest 10% of flows, respectively.

Constituents whose major source is deposition include sodium and chloride. These are largely unreactive within the catchment and only major sea-salt deposition episodes (e.g. winter 1990, Figure 2) produce a large stream

*Table 2.* Rainfall weighted mean concentrations and loads of non-marine sulphate and nitrate-nitrogen at the Afon Hafren for the 5 years from January 1989 to January 1994.

| Concentrations (µEq/l) | Plynlimon | Mid Wales | [1]UK range |
|---|---|---|---|
| Sulphate | 26.6 | 20–40 | <20 to >100 |
| Nitrate | 18.2 | 10–20 | <10 to >40 |
| Ammonium | 16.7 | 20–30 | <10 to >50 |
| **Fluxes ($gm^2y^{-1}$)** | **Plynlimon** | **Mid Wales** | **UK range** |
| Sulphate | 1.02 | 0.6–0.9 | <0.3 to >1.2 |
| Nitrate | 0.61 | 0.3–0.4 | <0.2 to >0.5 |
| Ammonium | 0.58 | 0.3–0.6 | <0.2 to >0.6 |

[1] Cf. Vincent *et al.*, (1995)

response followed by an exponential decline to concentrations approaching the mean value (Fig. 4). This demonstrates the hydrological complexity of the catchments and run-off processes; it also gives an indication of the mean residence time of water within the catchment. Deposition falling directly on to the stream or the near-stream zone results in a sharp increase in concentration; water falling onto the catchment farther from the stream is subject to longer travel times and greater mixing and dilution by older water stored within the catchment, as well as dilution by subsequent deposition of lower salt concentration. This effectively damps, or integrates-out, the variations observed in rainfall and explains the slow decline in concentration following such an event. Long-term variations in chloride and sulphur concentrations in the Afon Hafren indicate variations in depositional processes associated with weather patterns (Fig. 4). The high chloride periods coincide with Atlantic frontal systems and high sulphur periods coincide with easterly air masses bringing pollution from industrial areas.

Other components derived predominantly from, or heavily influenced by, atmospheric inputs are copper, chromium, fluoride and, to a lesser extent, boron (Fig. 3, Appendix Fig. 1); their stream concentration patterns follow those in deposition more closely. Not all of the observed peaks in deposition concentrations are observed in the streams because these peaks are often associated with very small rainfall volumes. In the case of chromium, the enhanced rainfall concentration period from 1992 onwards is not seen in the stream. This is probably associated with a highly reactive form of Cr which is then imbibed by catchment (see Neal *et al.*, 1996).

Those constituents of stream water that are controlled largely by in-catchment processes fall into groupings associated with their sources, chemical and biological processes, and the physical structure of the catchments. This physical structure of the catchment in turn affects the hydrological pathways delivering different proportions of chemically different waters to the stream at any one time. For example, at baseflow, stream waters have higher calcium and silicon concentrations and alkalinities than stormflow waters (Fig. 5).

These baseflow waters are derived from acidic soil waters that have followed slow and deep transport pathways within the catchment entering the lower soil horizons and the groundwater system which has been discovered to be extensive at Plynlimon (see Neal, 1997; Neal *et al.*, 1997; Hill and Neal, 1997). The bedrock, consisting of weatherable and acid-soluble inorganic components such as calcite and layer lattice silicates (chlorite and illite), has the capacity to neutralise these acid waters and precipitate the easily hydrolysable transition metals and aluminium. Such reacted water degasses carbon dioxide on its passage to the stream and produces the characteristic low acidity base flow chemistry which is rich in calcium and silica, but depleted in aluminium and transition metals.

Variations in bedrock composition lead to the differences in stream water chemistry of the Afon Hafren and Afon Hore. The presence of calcite and lead/zinc sulphides in the Hore catchment leads to high calcium

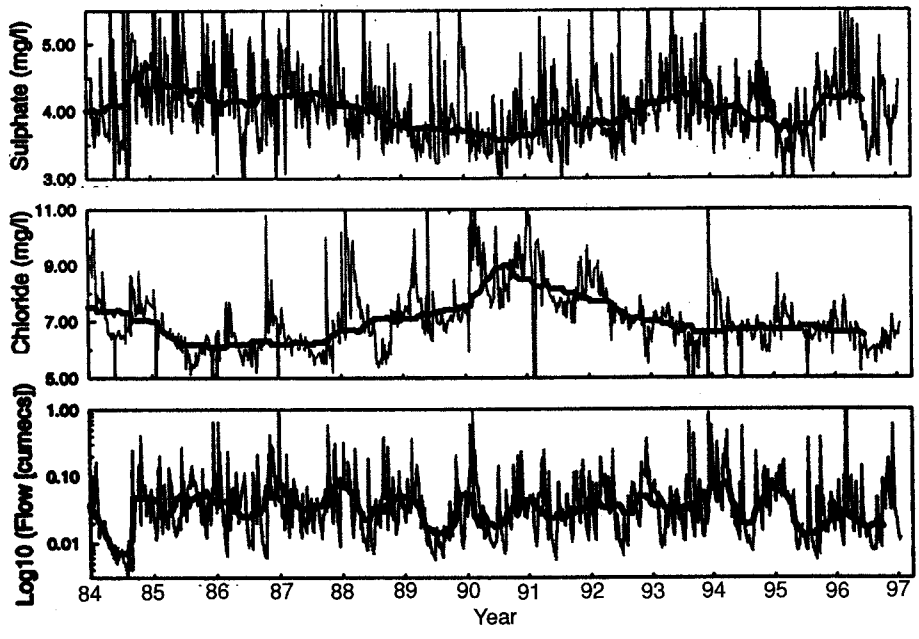


Fig. 4. *Time series of sulphate, chloride and flow in the Afon Hafren. Thick lines are 100 day ($SO_4$, Cl) and 30 day (flow) running medians.*

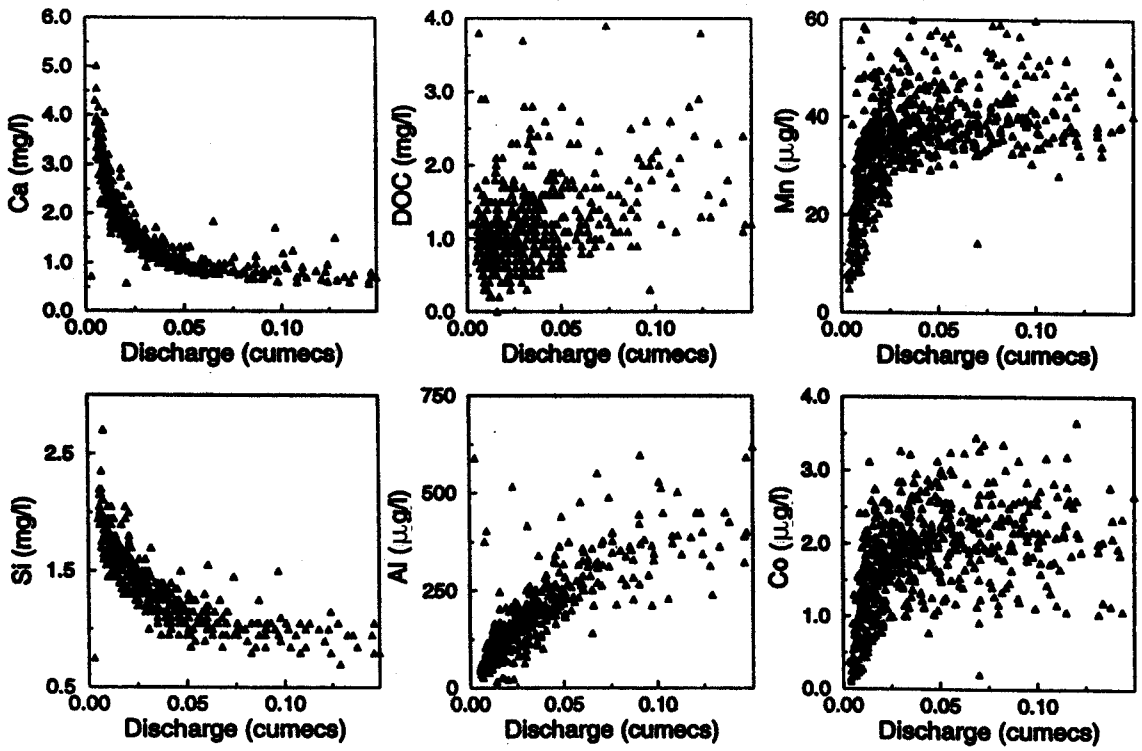


Fig. 5. *Plots of calcium, silicon, DOC, aluminium, manganese and cobalt concentrations against flow for the upper Afon Hore.*

concentrations and measurable lead concentrations in the stream (a factor of four or more difference between the two streams: Appendix Tables 3 and 4). Other differences in bedrock composition lead to contrasting behaviours of strontium and magnesium for the two catchments. Concentrations of lead and zinc in the Afon Hore are lowest under baseflow conditions. Thus, either the parent sulphides in the bedrock are not oxidized to soluble forms or there is an unidentified ion exchange or solubility control in the groundwater.

Stormflow waters, in contrast, have higher aluminium, DOC, yttrium, manganese, cobalt, nickel, beryllium and hydrogen ion concentrations than those at baseflow. The major concentration changes occur at relatively low flows: at intermediate to high flows, concentrations remain either constant or decline as flow increases (Figure 5). This difference reflects the large chemical gradients between soil and bedrock within the catchments and the different flow paths followed by water under drier and wetter conditions. Artificial drought periods have been shown to generate soilwaters very high in DOC; at drought-break, this soil water is flushed into the streams (Mitchell and MacDonald, 1992). This drying/wetting effect has been observed in the Plynlimon streams and accounts for the seasonal cycles observed in DOC and associated species such as iron, boron, bromide and iodine (Figure 6, Appendix Fig. 1). These cycles are driven by the microbial decomposition of organic matter in the peaty soils of the catchments. Stream concentrations of these constituents are at their lowest in winter and spring when the soils are cool and wet and microbial activity is at a minimum. Concentrations rise towards the end of the summer into autumn. During the summer, dryer conditions and higher temperatures accelerate the breakdown of organic matter into mobile components, ready to be flushed into the streams with the first autumn storms. In streams with a much higher proportion of peat cover, DOC concentrations are much higher than at Plynlimon and peak around mid-winter (Eatherall, 1996). The difference in patterns at Plynlimon is due to the flushing and, later in the season, dilution of soil waters by the high volumes of rainfall received during the winter and spring period.

For DOC, bromide and iodine, there has been a steady increase in concentration through the years and this probably coincides with a general increase in colour within the uplands reported informally by Environment agency staff.

Manganese and cobalt are two constituents whose concentrations rise with flow, but, unlike DOC, there is little biological influence on their concentrations and the cyclic seasonal variation in concentration is less apparent (Appendix Fig. 1). The amount of these constituents reaching the stream is determined purely by wetting and drying of gleyed layers within the soil and the transition from immobile to mobile forms. The concentrations of manganese and cobalt rise sharply at low to intermediate flows and then plateau and may decline at even higher

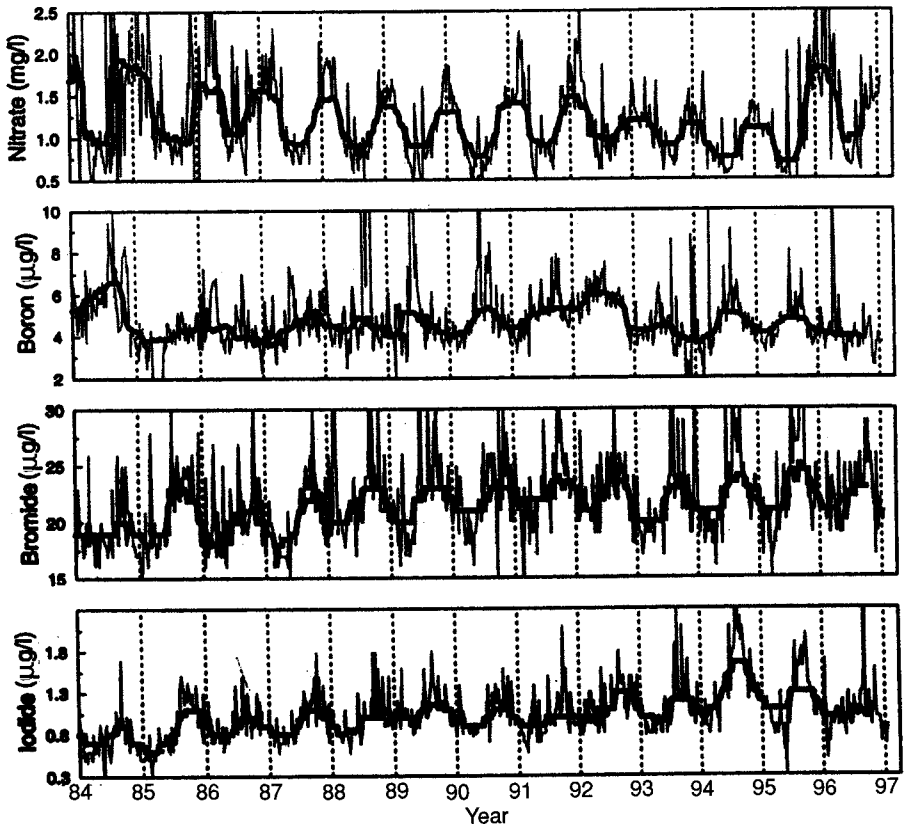


Fig. 6. *Time series plots of nitrate, boron, bromide and iodine for the Afon Hafren. Thick lines are 30 day running medians.*

flows. This pattern may again result from physical aspects of the catchments; gleyed areas tend to lie at the stream margins in valley floor areas; these are zones of hydrological convergence and will tend to be the first areas to wet-up. Once wetted-up, the supply of new source areas for these species will be relatively small. Aluminium, however, is derived throughout the upper soil system and its rise in concentration with flow is more gradual and continues up to high flows. With intense and long duration storms, at the very highest flows, there may be infiltration excess or saturation excess run-off, resulting in dilution of the soil-derived constituents and declining concentrations of aluminium and other species.

Other solutes involved in biological cycles include the nutrient components nitrate and potassium. These constituents are active in current nutrient cycles between the forest and soil ecosystem. Boron, bromide and iodine, associated with DOC are perhaps associated with a longer term break-down of ancient peat caps on the upper areas of the catchments. Their concentrations do not follow those of nitrate and potassium which leach from the catchments when there is a deficit of nutrient uptake by the forest, i.e. during the winter, outwith the growing season. In the spring and summer, plant uptake reduces the amount of loss via microbial decomposition and the concentrations observed in the streams are lower (Fig. 6).

## IMPACTS OF LARGE SCALE CLEAR-FELLING

The most marked changes in stream water chemistry associated with felling in the Hore catchment were increases in concentrations of three nutrients; nitrate, potassium and bromide (Fig. 7 and Appendix Fig. 1). Such increases commonly last for 3 to 5 years after which concentrations return to background levels. In the Hore, the extended period of felling operations meant that the increased nutrient concentrations persisted for 8 years. The increased nutrient concentrations following tree felling result from a combination of processes. Firstly, the decomposition of brash and stumps releases potassium (and dissolved organic carbon) with either a decrease or an increase in nitrate depending upon circumstances. Secondly, there is a break in the nutrient cycle as there is no longer uptake by the trees; this leads to more potassium and nitrogen being available for leaching. Thirdly, there is increased mineralization of organic matter leading to the soil water being supplied with additional dissolved organic carbon and organic nitrogen. Nitrate supplies also increase due to the nitrification of ammonium, and the breakdown of the brash is not sufficiently rapid to remove nitrate by fungal and microbial processes. The presence of brash on the catchment also limits development of vegetation which would take up nutrients. A further less obvious change is

in the timing of the peak nutrient concentrations. Prior to felling, nitrate and potassium concentrations peaked in mid to late winter and after felling in early to mid-winter (a phase shift of between 1 to 2 months). This was not the case for bromide concentrations which peaked in late summer to autumn; the elevated concentrations are more likely to result from the drying and warming of the upper soil layers resulting in enhanced organic matter breakdown.

Other changes in chemistry are more subtle (Figure 8) and may be summarized as:

1. The reduction of solute capture from mist and dry deposition. The concentration of solutes whose major source is deposition fall in concentration following felling. Chloride concentrations prior to felling were greater in the lower forested part of the Hore catchment compared to the partly moorland-covered upper Hore. After felling, the chloride concentration in the Hore fell to that in the upper Hore, eventually (after 8 years) falling below that of the upper Hore. The absence of the rough forest canopy reduces capture of sea-salts and pollutants from mist and dry deposition compared to the control stream (see Wilkinson *et al.*, 1997): the reduction is around 25% for most constituents: this part of the catchment lies at a lower altitude, further reducing the potential to capture mist and dry deposition. The time delay between felling of the catchment and the reduction of chloride concentrations below those in the upper Hore is probably due to long-term storage in the catchment and the time taken for the system to equilibrate to the reduced input of chloride.
2. Dissolved organic carbon concentrations increased slightly with felling. The general disturbance of the land leads to greater solution of organic components; hydrological conditions changed so that more water is supplied from the organic-laden upper soil layers. The micro climate changed with felling, with the loss of tree shade increasing soil temperature (up to 3°C higher in summer, Fig. 7) and thus the rate of organic matter decomposition increased. This change has persisted throughout the period of record following felling.
3. Transient acidification and enhanced aluminium leaching. The amplitude of the seasonal cycles of aluminium in the Hore was enhanced for the first 2 years following harvesting; the main increases occurred during the winter period when aluminium concentrations were at their highest. This indicated that the release of

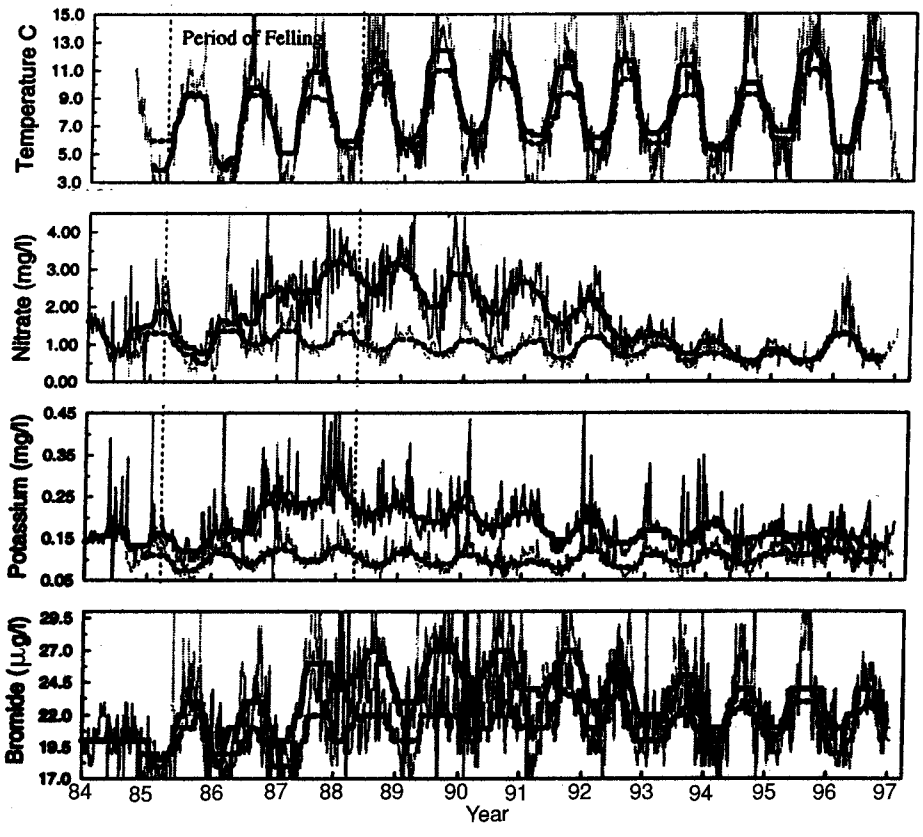


Fig. 7. *Time series plots of stream temperature, nitrate, potassium and bromide for the moorland upper Afon Hore (dotted line) and the Afon Hore (solid line) clear-felled from 1985 to 1988.*

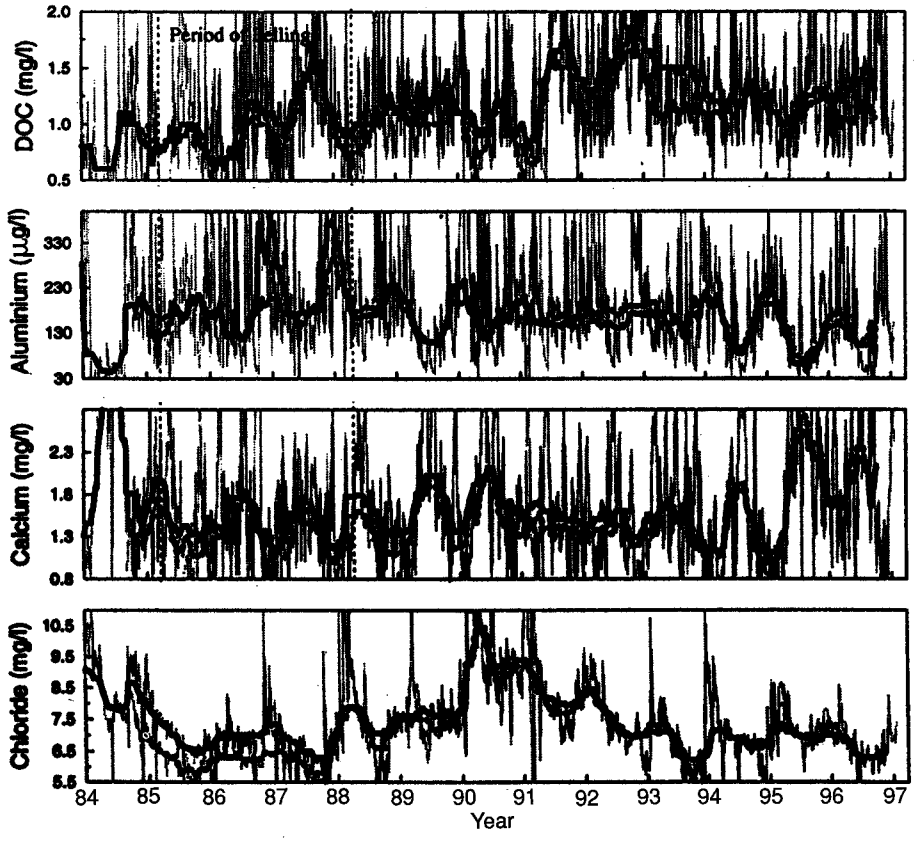


Fig. 8. *Time series plots of DOC, aluminium, calcium and chloride for the upper Afon Hore (dotted line) and the Afon Hore (solid line) clear-felled from 1985 to 1988.*

aluminium from the soils was due to increased nitrate concentrations displacing aluminium from exchangeable cation sites and leaching hydrous phases in the soil. The increase in aluminium, like nitrate, was only transient; concentrations have now fallen below those from the upper part of the catchment and this may again reflect the reduced capture of acidic deposition. There was also a reduction in the concentration of calcium in the Hore for the first few years after felling. This recovered briefly then fell again, merging with the concentration in the upper Hore towards the end of the period of record. A number of factors may account for these changes and may explain why the aluminium concentration was elevated only briefly. Firstly, the reduction of base cation capture from the atmosphere, combined with the nitrate release has a doubly acidifying affect. Brash break-down two to three years after felling may explain the minor recovery in calcium concentration, offsetting the effects of nitrate release and reducing aluminium rise in this period. From 1991 onwards, the aluminium concentration in the Hore fell below that in the upper Hore, calcium concentration was higher in the Hore during this period and nitrate concentration was beginning to fall towards the concentration in the upper Hore. Thus, the acidifying phase of felling was complete by 1991. The continuation of lower calcium concentrations in the Hore may reflect a reduction in calcium from dry and mist deposition as well as a reduction in acidic inputs and a concomitant reduction in weathering.

## INPUT-OUTPUT BUDGETS

To compute input-output budgets, a simplified scheme has been undertaken following the more detailed work of Durand *et al.*, (1994) for the Plynlimon catchments. The long term flow weighted chemical data for rainfall, cloud-water and stream water has been compared, based on an average cloud-water input of chloride of 20% of the rainfall figure (Table 4; cf Durand *et al.*, 1994). From this, the percentage retention of the atmospheric input or net gain from the catchment has been determined for the streams, based on the assumption that there is a net chloride input-output balance (Table 5).

Six broad groups of chemical determinands can be distinguished:

*Table 3.* Baseflow and stormflow chemistries for the Afon Hafren, upper Afon Hore and Afon Hore (prior to felling).

| | | Lower Hafren | | Lower Hore | | Upper Hore | |
|---|---|---|---|---|---|---|---|
| | | Base | Storm | Base | Storm | Base | Storm |
| Na | mg/l | 4.1 | 3.8 | 4.2 | 3.9 | 3.8 | 3.6 |
| K | mg/l | 0.1 | 0.2 | 0.2 | 0.3 | 0.1 | 0.1 |
| Ca | mg/l | 0.9 | 0.7 | 1.8 | 0.8 | 1.6 | 0.5 |
| Mg | mg/l | 0.8 | 0.7 | 0.9 | 0.7 | 0.7 | 0.6 |
| $SO_4$ | mg/l | 4.1 | 4.5 | 4.9 | 4.5 | 3.7 | 3.8 |
| Si | mg/l | 1.7 | 1.0 | 1.6 | 0.9 | 1.4 | 0.8 |
| DOC | mg/l | 1.3 | 2.8 | 1.2 | 2.5 | 1.1 | 2.2 |
| $NO_3$ | mg/l | 1.2 | 1.5 | 1.7 | 1.9 | 1.1 | 1.1 |
| $NH_4$ | mg/l | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $PO_4$ | mg/l | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| F | mg/l | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Cl | mg/l | 7.2 | 7.1 | 7.6 | 7.3 | 7.0 | 7.3 |
| pH | | 5.4 | 4.5 | 5.9 | 4.6 | 6.0 | 4.5 |
| Acid | μeq/l | 126.5 | 217.6 | 129.5 | 172.6 | 134.7 | 200.3 |
| Alk | μeq/l | 0.2 | −33.6 | 33.6 | −23.1 | 37.0 | −34.2 |
| Cond | μS | 41.9 | 49.5 | 47.9 | 48.3 | 41.9 | 48.8 |
| Mn | μg/l | 36.0 | 43.6 | 33.1 | 36.0 | 22.8 | 20.1 |
| Fe | μg/l | 76.4 | 127.1 | 65.1 | 106.6 | 77.0 | 87.1 |
| Li | μg/l | 2.0 | 1.8 | 2.1 | 1.9 | 1.8 | 1.5 |
| Be | μg/l | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| B | μg/l | 5.2 | 5.8 | 5.6 | 5.8 | 4.9 | 4.8 |
| Al | μg/l | 174.0 | 416.3 | 189.3 | 474.9 | 195.1 | 463.9 |
| Cr | μg/l | 2.6 | 2.5 | 2.6 | 1.8 | 4.3 | 4.4 |
| Ni | μg/l | 2.0 | 2.4 | 2.4 | 2.8 | 1.6 | 1.6 |
| Co | μg/l | 1.7 | 2.0 | 1.8 | 2.0 | 1.6 | 1.6 |
| Cu | μg/l | 1.7 | 3.3 | 2.0 | 3.2 | 1.9 | 2.8 |
| Zn | μg/l | 14.1 | 20.0 | 20.7 | 27.0 | 13.9 | 17.0 |
| Sr | μg/l | 5.3 | 4.8 | 5.8 | 4.5 | 4.8 | 3.7 |
| Y | μg/l | 0.3 | 0.4 | 0.2 | 0.4 | 0.2 | 0.3 |
| Ba | μg/l | 3.0 | 4.7 | 4.4 | 5.8 | 2.8 | 3.1 |
| Pb | μg/l | 1.6 | 1.7 | 4.1 | 8.7 | 5.4 | 12.1 |
| Br | μg/l | 21.6 | 24.5 | 23.4 | 25.0 | 21.0 | 22.1 |
| I | μg/l | 1.0 | 1.3 | 0.9 | 1.3 | 0.9 | 1.1 |

1. Determinands which are strongly retained by the catchment: ammonium, iodine and lead. For these determinands, ammonium acts as a fertilizer to the vegetation and is easily converted to nitrogen in higher oxidation states such as nitrate (Miegroet and Johnson, 1993). Iodine is a nutrient and is easily assimilated into organic matter both by inorganic and organic processes (Neal, 1990c). Lead is unusual in that, as discussed earlier, it has entered the catchment in significant concentrations only in recent years. It is not clear what the form of this lead is, but lead is rapidly adsorbed by vegetation and organic rich soils (Salmons and Forstner, 1984). The uptake of lead is much higher in the Hafren than in the Hore; this is associated with the within catchment supplies in the Hore, available from the much higher bedrock mineralization, as already noted.
2. Determinands which are partially retained by the catchment: phosphate, boron, barium, bromide and nitrate. Apart from barium, these determinands are nutrients and some retention by the catchments would be expected as in the first case (Lindsay, 1972; Price *et al.*, 1972). In the case of nitrate, there is a net release from the Hore catchment and this reflects the effects of felling as discussed earlier in the paper. The pattern for barium is unexpected and it seems that the properties of this element differ from the other divalent base cations and that barium is involved as a trace nutrient.
3. Determinands showing a net input–output balance:

*Table 4.* Input-output data for the Hafren and Hore catchments.

| | | Rain | Cloud | Input | Hafren | Upper Hore | Lower Hore |
|---|---|---|---|---|---|---|---|
| Na | mg/l | 2.30 | 26.69 | 2.92 | 3.84 | 3.99 | 4.10 |
| K | mg/l | 0.12 | 1.11 | 0.14 | 0.19 | 0.12 | 0.30 |
| Ca | mg/l | 0.19 | 1.86 | 0.24 | 0.72 | 0.92 | 1.12 |
| Mg | mg/l | 0.28 | 3.15 | 0.35 | 0.69 | 0.63 | 0.81 |
| $NH_4$ | mg/l | 0.29 | 3.39 | 0.37 | 0.01 | 0.01 | 0.02 |
| Cl | mg/l | 4.33 | 45.88 | 5.39 | 6.91 | 7.52 | 7.76 |
| $SO_4$ | mg/l | 1.57 | 14.20 | 1.90 | 4.21 | 3.94 | 4.70 |
| $NO_3$ | mg/l | 0.77 | 11.41 | 1.04 | 1.32 | 0.98 | 2.69 |
| $PO_4$ | mg/l | 0.02 | 0.04 | 0.02 | 0.03 | 0.01 | 0.02 |
| F | mg/l | 0.02 | 0.04 | 0.02 | 0.05 | 0.05 | 0.06 |
| DOC | mg/l | 0.48 | 1.72 | 0.52 | 2.26 | 1.89 | 1.65 |
| Si | mg/l | 0.10 | 0.07 | 0.10 | 1.20 | 0.98 | 1.13 |
| Al | μg/l | 6.22 | 45.20 | 7.26 | 310.69 | 336.27 | 427.52 |
| B | μg/l | 3.16 | 80.15 | 5.00 | 5.23 | 4.61 | 5.35 |
| Ba | μg/l | 4.92 | 5.30 | 5.04 | 4.50 | 4.14 | 6.38 |
| Be | μg/l | 0.01 | 0.03 | 0.01 | 0.08 | 0.08 | 0.11 |
| Br | μg/l | 16.36 | 142.63 | 19.65 | 23.43 | 21.46 | 24.27 |
| Co | μg/l | 0.04 | 0.16 | 0.04 | 1.87 | 1.57 | 2.42 |
| Cr | μg/l | 1.66 | 0.52 | 1.67 | 2.48 | 1.96 | 3.73 |
| Cu | μg/l | 1.47 | 5.18 | 1.59 | 2.75 | 2.59 | 2.90 |
| Fe | μg/l | 5.78 | 39.11 | 6.68 | 109.92 | 88.20 | 88.17 |
| I | μg/l | 1.16 | 8.61 | 1.36 | 1.22 | 1.04 | 1.04 |
| Li | μg/l | 0.08 | 0.59 | 0.09 | 1.98 | 1.81 | 2.17 |
| Mn | μg/l | 1.06 | 9.45 | 1.28 | 40.21 | 20.33 | 39.72 |
| Ni | μg/l | 0.46 | 2.14 | 0.51 | 2.23 | 1.82 | 2.79 |
| Pb | μg/l | 13.73 | 12.56 | 14.02 | 1.53 | 10.79 | 7.72 |
| Sr | μg/l | 2.00 | 21.39 | 2.49 | 4.92 | 4.15 | 5.39 |
| Y | μg/l | 0.01 | 0.05 | 0.01 | 0.36 | 0.31 | 0.30 |
| Zn | μg/l | 8.59 | 57.82 | 9.92 | 17.55 | 16.00 | 25.24 |
| pH | | 4.99 | 4.98 | 5.11 | 4.82 | 5.10 | 5.00 |
| $Alk_{Gran}$ | μeq/l | −12.67 | −45.45 | −13.72 | −20.96 | −7.81 | −10.33 |

chloride (by definition), sodium and possibly chromium. Sodium and chloride are, chemically, relatively unreactive in the catchment and a long term net input-output balance would be expected. For chromium, the situation is more complex as it occurs in two oxidation states, one having low chemical reactivity (CrVI in the form of chromate) and the other (CrIII) which is adsorbed by the soil. A detailed discussion of this element is given in Neal *et al.*, (1996); it seems that, throughout the 1980s, the main input has been as CrVI but that for the last few years CrIII has predominated and has an association with lead pollution in rainfall.

4. Determinands showing a net output which is modest and up to 70% of the input: calcium, magnesium, sulphate, fluoride, DOC, copper, strontium and zinc. For these determinands, there are relatively important atmospheric and within catchment sources and sinks. For example, magnesium, calcium and strontium have maritime sources; in addition they provide major base cation weathering sources from both carbonates and silicate minerals within the bedrock (Neal *et al.*, 1997a,b). For DOC, the main catchment sources are from breakdown of organic matter and the generation of humic and fulvic acids. The input-output balance of sulphate is more complex to determine as there are significant gaseous inputs to the catchment from acidic oxides ($SO_x$). Indeed, there may well be a net balance if the gaseous term is included (cf Durand *et al.*, 1994; Wilkinson *et al.*, this volume).
5. Determinands showing a major net output (>70%): aluminium, silicon, beryllium, cobalt, iron, lithium, manganese, nickel and yttrium. These determinands represent two distinct hydrochemical groupings. Firstly, silicon and lithium are derived from the weath-

*Table 5.* Catchment water quality percentage balances for the Hafren and Hore catchments.

| | Hafren | Upper Hore | Lower Hore |
|---|---|---|---|
| Na | 3 | –2 | –3 |
| K | 3 | –67 | 30 |
| Ca | 58 | 64 | 70 |
| Mg | 35 | 22 | 38 |
| $NH_4$ | –3103 | –5468 | –2084 |
| Cl | 0 | 0 | 0 |
| $SO_4$ | 42 | 33 | 42 |
| $NO_3$ | –1 | –48 | 45 |
| $PO_4$ | –5 | –96 | –44 |
| F | 51 | 48 | 54 |
| DOC | 71 | 62 | 55 |
| Si | 89 | 86 | 87 |
| Al | 97 | 97 | 98 |
| B | –23 | –51 | –35 |
| Ba | –44 | –70 | –14 |
| Be | 85 | 85 | 89 |
| Br | –8 | –28 | –17 |
| Co | 97 | 96 | 97 |
| Cr | 14 | –19 | 36 |
| Cu | 26 | 14 | 21 |
| Fe | 92 | 89 | 89 |
| I | –43 | –82 | –88 |
| Li | 94 | 93 | 94 |
| Mn | 96 | 91 | 95 |
| Ni | 71 | 61 | 74 |
| Pb | –1073 | –81 | –162 |
| Sr | 35 | 16 | 33 |
| Y | 96 | 95 | 95 |
| Zn | 28 | 13 | 43 |
| $Alk_{Gran}$ | 16 | –145 | –91 |

ering of the bedrock. Secondly, the remaining determinands are metals which exist as highly charged or complexed species in solution and which are easily hydrolysed in the environment. These metals occur predominantly within the hydrous-oxides and oxides within the soil and they are mobilized under acidic conditions (Salmons and Forstner, 1984).

6. Determinands showing a variable response: potassium and alkalinity. Potassium is a nutrient component and exists as a weatherable source within micaceous minerals within the soil and bedrock. For the Hafren, there seems to be a net balance between biological uptake and weathering release; for the upper Hore, the biological uptake predominates. For the lower Hore, there is a net release, but this would be anticipated given the disruption of the biological cycle with felling. For alkalinity, there is a high net production by the catchment for the upper and lower stretches of the Hore and this is characteristic of the effects of the higher bedrock weathering rates for this catchment. For the Hafren, where easily weatherable minerals are less abundant, there is a much closer balance between input and output although no allowance has been made for the acidity within the input associated with gaseous acidic oxides which would increase the estimate of net alkalinity production.

## Summary

Despite the apparent distance from industrial areas, the Plynlimon catchments experience atmospheric pollution by both acidic oxides and heavy metals. The extent of this pollution varies according to air mass trajectories and the patterns of change seem to be cyclical in nature. Load calculations based on bulk deposition at Plynlimon show no reduction in the deposition of acidic pollutants (Table 6) despite reduced industrial production and the greater emission controls imposed in the last 20 years. In the case of metals such as chromium and lead, unexpected atmospheric pollution episodes were observed. In the case of chromium, concentrations were highest in the mid 1980s; this timing does not tally with the other industrial pollutants and the source of this pollution remains unknown. For lead, the increases in concentration in the last few years may well be associated with increased car rallying in the area (Wilkinson and Jenkins, 1996).

In the streams, the patterns of water quality variations match three dominant hydrobiogeochemical controls as well as a composite pattern.

1. *Weathering and inorganic leaching.* The components which fit into this group have the largest catchment supplies (as indicated by the input-output balances) and

*Table 6.* Annual rainfall weighted mean concentrations and loads of non-marine sulphate and nitrate-nitrogen from bulk deposition data at Plynlimon.

| | $SO_4$* μeq/l | kg-S/Ha/yr | $NO_3$-N μeq/l | kgN/Ha/yr |
|---|---|---|---|---|
| 1984 | 35.5 | 11.6 | 24.6 | 7.1 |
| 1985 | 28.8 | 9.3 | 22.8 | 6.4 |
| 1986 | 22.7 | 9.4 | 18.3 | 6.6 |
| 1987 | 24.6 | 8.9 | 16.4 | 5.2 |
| 1988 | 22.3 | 9.3 | 19.8 | 7.2 |
| 1989 | 25.7 | 9.4 | 19.7 | 6.3 |
| 1990 | 20.6 | 7.9 | 18.7 | 6.2 |
| 1991 | 24.1 | 9.6 | 15.3 | 5.3 |
| 1992 | 28.0 | 11.3 | 17.0 | 6.0 |
| 1993 | 33.7 | 12.3 | 20.1 | 6.4 |
| 1994 | 27.1 | 12.2 | 17.9 | 7.0 |
| 1995 | 29.1 | 9.7 | 17.3 | 5.0 |

they show the greatest variations with flow. The components divide into two groups (1a and 1b). Firstly, in group 1a, there are several base cations (Ca, Sr, Li), silica and bicarbonate (as represented by high alkalinities) which have highest concentrations under baseflow conditions. These components are derived from reactions occurring within the bedrock and groundwater zones. Secondly, in group 1b, there are several transition metals (Co, Fe, Mn, Ni) and beryllium, aluminium and yttrium which have their highest concentrations at intermediate to peak flows (group 1b). This second group comprises elements which are readily hydrolysable, are mobilized under acidic conditions and precipitate under more basic conditions. They are derived essentially from the breakdown of oxides and hydroxides within the acidic soil zones and in some cases the leaching rate and stability in solution may be augmented by complexation with fluorides, hydroxyl ions and organic acids. In terms of the input-output relationships, the second group show the highest percentage catchment sources due to the increased flux contribution at high flows.

2. *Biological mediation.* The components which fit into this group are the nutrients (ammonium, nitrate, phosphate, bromide, boron and iodine). With the exceptions of phosphate and ammonium, all of these components show a strong seasonality and accumulate in or leak from the catchment. There is no significant phosphate or ammonium supply within the bedrock and it seems that virtually all these components are retained within the biomass, or, in the case of ammonium, converted to other forms of nitrogen.
3. *Physical controls.* This group comprises the components which have a predominant atmospheric source and little within-catchment reactivity. The main elements in this group are the marine components sodium and chloride. For this group, there is little relationship between concentration and flow and a net input-output balance is observed (except for sulphate where an additional gaseous input has not been allowed for). However, also in this group is chromium (for the 1980s), where the atmospheric source is probably the unreactive species chromate, and sulphate.
4. *Composite controls.* This group consists of zinc and lead where there are significant atmospheric inputs which are partially retained (for zinc) or almost completely retained (for lead) by the catchment. But, at the same time, they are also generated within the catchment to augment stream water concentrations. For both of these transition metals, stream water concentrations are highest under storm flow. This would be expected given the similarity in their hydrochemical properties to the group 1b elements described above.

With forest felling, the disruption of the biological system has increased the supply of nutrients to the stream and led to a transient increase in aluminium concentrations. These results are good news for forestry management in terms of upland water quality in that the effects of even a major clear-felling programme are not long lived and, no apparently major environmental problems are caused. For example, deforestation has not led to appreciable increases in heavy metal pollutants. Indeed, the additional light afforded by the removal of tree shading may well have resulted in an improvement in stream biology with the return of the acid sensitive mayfly.

## Conclusions

The results of this study demonstrate behaviour consistent with current hydrobiogeochemical understanding. However, the longer term information reveals surprising features such as changing meteorological effects on pollutant inputs, the occurrence of heavy metal pollutant episodes and the effects of drought years on water quality. None of these longer term features would be predicted easily from current environmental impact models and none would be noticed with less than a decadal scale monitoring programme. While an understanding of general hydrochemical behaviour is of value to the research community, this longer term perspective is of profound environmental importance given that the UK climate is becoming more variable (Marsh and Sanderson, 1997) and that the UK industrial and agricultural base is changing with knock-on effects on pollutant emissions and river water quality patterns (Smith *et al.*, 1997; Neal *et al.*, 1997d).

There are few research programmes in the UK which have undertaken such extensive and detailed monitoring of deposition and runoff chemistry in the uplands. Indeed, major research emphasis by the water industry has focused on lowland areas where there are perceived to be more pressing problems associated with pollution from agriculture, urbanisation and industry (cf Robson *et al.*, 1996; Robson and Neal, 1997; Neal *et al.*, 1997d). Apart from a few studies (Langan *et al.*, 1997), the other sources of pollution entering lowland streams mean that the results of these studies are inequitable with the climatic changes being observed in the uplands. This is a fundamental shortfall in UK environmental research and yet both the finance and the will for long-term monitoring is dwindling in favour of short-term regional networks. Such networks are sampled at much lower frequency, over shorter study periods and often sampling a limited range of determinands at a low analytical quality (Robson and Neal, 1996; Neal *et al.*, 1997e). The main advantage of shorter term studies is to funding agencies with short term objectives. However, the results of such short-term studies are unsound both in terms of identifying environmental variability and for testing current understanding of how the environment actually responds to change. It is therefore important that environmental planners recognise the importance and value of long-term monitoring programmes and ensure that this

invaluable scientific resource is maintained. Put another way, we know far less about the hydrochemical functioning of our upland environments than currently used atmospheric and catchment environment models imply and the only true test of the limits of our environmental understanding lies in the direct and continued measurement of our environment.

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# Appendix

*Appendix Table 1.* Major, minor and trace element summary for rainfall.

| | | min | max | low vol | high vol | avg | fl avg |
|---|---|---|---|---|---|---|---|
| Na | mg/l | 0.00 | 23.60 | 2.32 | 2.73 | 2.07 | 2.30 |
| K | mg/l | 0.00 | 1.95 | 0.25 | 0.11 | 0.13 | 0.12 |
| Ca | mg/l | 0.00 | 4.60 | 0.90 | 0.16 | 0.29 | 0.19 |
| Mg | mg/l | 0.00 | 2.98 | 0.31 | 0.32 | 0.26 | 0.28 |
| $NH_4$ | mg/l | 0.00 | 4.10 | 0.93 | 0.16 | 0.45 | 0.29 |
| Cl | mg/l | 0.30 | 44.00 | 5.32 | 5.09 | 4.13 | 4.33 |
| $SO_4$ | mg/l | 0.00 | 15.90 | 4.00 | 1.26 | 2.00 | 1.57 |
| $NO_3$ | mg/l | 0.00 | 11.30 | 3.18 | 0.35 | 1.28 | 0.77 |
| F | mg/l | 0.00 | 0.23 | 0.04 | 0.02 | 0.02 | 0.02 |
| DOC | mg/l | 0.00 | 3.90 | 1.39 | 0.38 | 0.69 | 0.48 |
| $PO_4$ | mg/l | 0.00 | 1.22 | 0.02 | 0.02 | 0.03 | 0.02 |
| Si | mg/l | 0.00 | 3.95 | 0.15 | 0.06 | 0.11 | 0.10 |
| Al | μg/l | 0.00 | 176.40 | 35.78 | 3.24 | 11.68 | 6.22 |
| B | μg/l | 0.00 | 99.42 | 12.36 | 2.60 | 4.35 | 3.16 |
| Ba | μg/l | 0.00 | 246.53 | 22.59 | 4.68 | 8.02 | 4.92 |
| Be | μg/l | 0.00 | 0.24 | 0.01 | 0.01 | 0.01 | 0.01 |
| Br | μg/l | 1.00 | 128.00 | 19.24 | 18.90 | 15.50 | 16.36 |

| | | min | max | low vol | high vol | avg | fl avg |
|---|---|---|---|---|---|---|---|
| Co | μg/l | 0.00 | 4.06 | 0.18 | 0.02 | 0.06 | 0.04 |
| Cr | μg/l | 0.00 | 41.67 | 5.49 | 1.34 | 2.45 | 1.66 |
| Cu | μg/l | 0.00 | 29.99 | 3.96 | 0.92 | 1.99 | 1.47 |
| Fe | μg/l | 0.00 | 136.90 | 25.34 | 2.79 | 9.48 | 5.78 |
| I | μg/l | 0.40 | 5.20 | 2.04 | 1.01 | 1.48 | 1.16 |
| Li | μg/l | 0.00 | 2.20 | 0.12 | 0.08 | 0.09 | 0.08 |
| Mn | μg/l | 0.00 | 27.62 | 5.61 | 0.44 | 1.85 | 1.06 |
| Ni | μg/l | 0.00 | 18.58 | 1.67 | 0.21 | 0.76 | 0.46 |
| Pb | μg/l | 0.00 | 1206.59 | 115.93 | 9.06 | 28.52 | 13.73 |
| Sr | μg/l | 0.00 | 19.00 | 3.67 | 2.24 | 2.16 | 2.00 |
| Y | μg/l | 0.00 | 0.24 | 0.04 | 0.01 | 0.01 | 0.01 |
| Zn | μg/l | 0.00 | 185.62 | 42.92 | 4.77 | 13.62 | 8.59 |
| pH | | 3.36 | 6.95 | 4.71 | 5.11 | 4.93 | 4.99 |
| $Alk_{Gran}$ | μeq/l | −436.52 | 201.14 | −42.01 | −8.42 | −18.59 | −12.67 |

*Appendix Table 2.* Major, minor and trace element summary for cloud-water.

| | | min | max | Small | High | avg | fl avg |
|---|---|---|---|---|---|---|---|
| Na | mg/l | 1.26 | 1034.20 | 85.50 | 22.96 | 40.92 | 26.69 |
| K | mg/l | 0.08 | 44.00 | 3.78 | 1.90 | 1.89 | 1.11 |
| Ca | mg/l | 0.16 | 107.10 | 9.62 | 5.40 | 4.34 | 1.86 |
| Mg | mg/l | 0.12 | 130.50 | 10.76 | 2.99 | 5.04 | 3.15 |
| $NH_4$ | mg/l | 0.14 | 49.00 | 8.98 | 6.01 | 6.20 | 3.39 |
| Cl | mg/l | 1.70 | 740.00 | 32.39 | 45.06 | 56.06 | 45.88 |
| SO4 | mg/l | 0.93 | 510.40 | 48.55 | 24.77 | 25.86 | 14.20 |
| $NO_3$ | mg/l | 0.45 | 180.00 | 29.93 | 21.24 | 23.06 | 11.41 |
| $PO_4$ | mg/l | 0.00 | 0.91 | 0.14 | 0.08 | 0.10 | 0.04 |
| F | mg/l | 0.00 | 0.69 | 0.13 | 0.08 | 0.08 | 0.04 |
| DOC | mg/l | 0.00 | 23.00 | 4.00 | 2.81 | 2.93 | 0.07 |
| Si | mg/l | 0.00 | 0.95 | 0.10 | 0.15 | 0.08 | 1.72 |
| Al | μg/l | 0.00 | 5891.56 | 461.12 | 267.11 | 162.09 | 45.20 |
| B | μg/l | 0.00 | 4930.00 | 102.29 | 54.93 | 116.34 | 80.15 |
| Ba | μg/l | 0.56 | 298.94 | 27.58 | 16.42 | 13.67 | 5.30 |
| Be | μg/l | 0.00 | 1.47 | 0.19 | 0.06 | 0.07 | 0.03 |
| Br | μg/l | 6.00 | 2300.00 | 110.48 | 160.84 | 176.51 | 142.63 |
| Co | μg/l | 0.00 | 15.66 | 1.26 | 0.56 | 0.45 | 0.16 |
| Cr | μg/l | 0.00 | 86.18 | 6.70 | 1.25 | 1.70 | 0.52 |
| Cu | μg/l | 0.16 | 427.42 | 28.02 | 17.48 | 12.91 | 5.18 |
| Fe | μg/l | 0.00 | 2332.00 | 191.85 | 188.20 | 109.93 | 39.11 |
| I | μg/l | 0.80 | 40.00 | 12.27 | 10.70 | 10.85 | 8.61 |
| Li | μg/l | 0.01 | 64.84 | 4.77 | 1.08 | 1.38 | 0.59 |
| Mn | μg/l | 0.00 | 1130.00 | 87.65 | 51.56 | 33.07 | 9.45 |
| Ni | μg/l | 0.00 | 234.71 | 16.87 | 4.94 | 5.44 | 2.14 |
| Pb | μg/l | 0.31 | 3384.14 | 204.40 | 45.10 | 47.38 | 12.56 |
| Sr | μg/l | 1.03 | 2506.34 | 161.37 | 29.24 | 45.67 | 21.39 |
| Y | μg/l | 0.00 | 19.26 | 0.91 | 0.17 | 0.20 | 0.05 |
| Zn | μg/l | 2.20 | 7155.51 | 387.01 | 122.95 | 128.59 | 57.82 |
| pH | | 2.68 | 6.88 | 4.38 | 4.96 | 4.62 | 4.98 |
| $Alk_{Gran}$ | μeq/l | −2089.30 | 734.00 | −164.94 | −118.74 | −112.11 | −45.45 |

*Appendix Table 3.* Major, minor and trace element summary for Afon Hafren water.

| | | min | max | base | storm | avg | fl avg |
|---|---|---|---|---|---|---|---|
| Na | mg/l | 2.27 | 5.70 | 4.07 | 3.70 | 4.05 | 3.84 |
| K | mg/l | 0.08 | 0.99 | 0.15 | 0.24 | 0.15 | 0.19 |
| Ca | mg/l | 0.32 | 2.34 | 1.07 | 0.62 | 0.87 | 0.72 |
| Mg | mg/l | 0.17 | 1.42 | 0.81 | 0.64 | 0.77 | 0.69 |
| $NH_4$ | mg/l | 0.00 | 0.55 | 0.02 | 0.03 | 0.01 | 0.01 |
| Cl | mg/l | 3.90 | 12.20 | 6.77 | 6.80 | 7.06 | 6.91 |
| $SO_4$ | mg/l | 2.17 | 12.27 | 3.59 | 4.30 | 4.10 | 4.21 |
| $NO_3$ | mg/l | 0.30 | 6.00 | 0.65 | 1.36 | 1.21 | 1.32 |
| $PO_4$ | mg/l | 0.00 | 0.45 | 0.08 | 0.02 | 0.04 | 0.03 |
| F | mg/l | 0.00 | 0.20 | 0.04 | 0.05 | 0.05 | 0.05 |
| DOC | mg/l | 0.00 | 7.30 | 0.90 | 2.98 | 1.45 | 2.26 |
| Si | mg/l | 0.50 | 4.60 | 2.09 | 0.90 | 1.60 | 1.20 |
| Al | μg/l | 24.41 | 1081.50 | 65.07 | 409.81 | 186.65 | 310.69 |
| B | μg/l | 0.00 | 71.40 | 5.33 | 5.68 | 5.06 | 5.23 |
| Ba | μg/l | 0.22 | 26.60 | 2.47 | 5.15 | 3.53 | 4.50 |
| Be | μg/l | 0.00 | 0.30 | 0.02 | 0.09 | 0.05 | 0.08 |
| Br | μg/l | 9.00 | 48.00 | 23.10 | 25.29 | 22.12 | 23.43 |
| Co | μg/l | 0.17 | 4.40 | 0.67 | 1.85 | 1.70 | 1.87 |
| Cr | μg/l | 0.00 | 51.20 | 2.48 | 2.43 | 2.35 | 2.48 |
| Cu | μg/l | 0.19 | 40.10 | 2.05 | 3.45 | 1.86 | 2.75 |
| Fe | μg/l | 22.81 | 295.80 | 63.24 | 132.31 | 82.53 | 109.92 |
| I | μg/l | 0.50 | 5.60 | 1.13 | 1.35 | 1.09 | 1.22 |
| Li | μg/l | 0.95 | 3.85 | 2.01 | 1.77 | 2.16 | 1.98 |
| Mn | μg/l | 7.40 | 127.90 | 19.66 | 43.15 | 36.36 | 40.21 |
| Ni | μg/l | 0.61 | 16.85 | 1.26 | 2.37 | 1.97 | 2.23 |
| Pb | μg/l | 0.00 | 120.79 | 1.42 | 1.71 | 1.17 | 1.53 |
| Sr | μg/l | 1.87 | 10.07 | 5.51 | 4.64 | 5.33 | 4.92 |
| Y | μg/l | 0.09 | 0.71 | 0.13 | 0.40 | 0.27 | 0.36 |
| Zn | μg/l | 3.28 | 115.50 | 12.96 | 20.51 | 14.81 | 17.55 |
| pH | | 4.12 | 6.83 | 6.47 | 4.50 | 5.39 | 4.82 |
| $Alk_{Gran}$ | μeq/l | −63.43 | 55.06 | 30.69 | −34.91 | −2.19 | −20.96 |

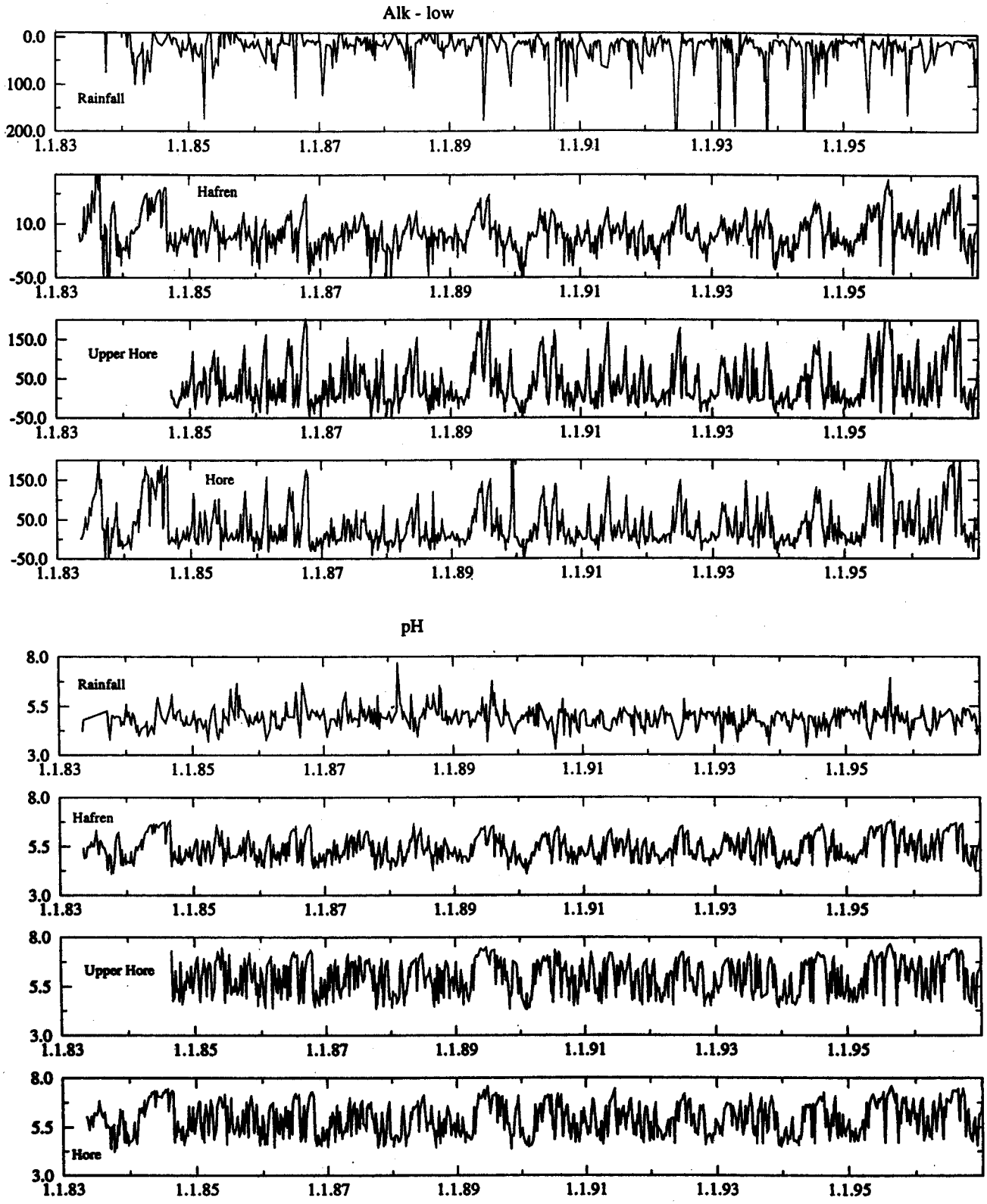
*Appendix Table 4.* Major, minor and trace element summary for upper Afon Hore water.

| | | min | max | baseflow | stormflow | avg | flow avg |
|---|---|---|---|---|---|---|---|
| Na | mg/l | 1.44 | 9.11 | 3.97 | 3.92 | 4.07 | 3.99 |
| K | mg/l | 0.00 | 0.38 | 0.11 | 0.12 | 0.11 | 0.12 |
| Ca | mg/l | 0.15 | 5.02 | 3.41 | 0.57 | 1.66 | 0.92 |
| Mg | mg/l | 0.16 | 1.35 | 0.90 | 0.57 | 0.73 | 0.63 |
| $NH_4$ | mg/l | 0.00 | 0.10 | 0.01 | 0.01 | 0.01 | 0.01 |
| Cl | mg/l | 3.80 | 20.00 | 6.88 | 7.42 | 7.42 | 7.52 |
| $SO_4$ | mg/l | 1.03 | 10.10 | 3.12 | 4.00 | 3.76 | 3.94 |
| $NO_3$ | mg/l | 0.20 | 3.60 | 0.68 | 0.97 | 0.94 | 0.98 |
| $PO_4$ | mg/l | 0.00 | 0.16 | 0.04 | 0.01 | 0.02 | 0.01 |
| F | mg/l | 0.00 | 0.20 | 0.05 | 0.05 | 0.05 | 0.05 |
| DOC | mg/l | 0.00 | 5.00 | 0.99 | 2.34 | 1.27 | 1.89 |
| Si | mg/l | 0.40 | 2.70 | 1.93 | 0.77 | 1.36 | 0.98 |
| Al | μg/l | 15.51 | 825.50 | 68.01 | 431.32 | 202.68 | 336.27 |
| B | μg/l | 1.35 | 63.00 | 5.00 | 5.21 | 4.60 | 4.61 |
| Ba | μg/l | 0.60 | 26.85 | 2.97 | 4.25 | 3.57 | 4.14 |

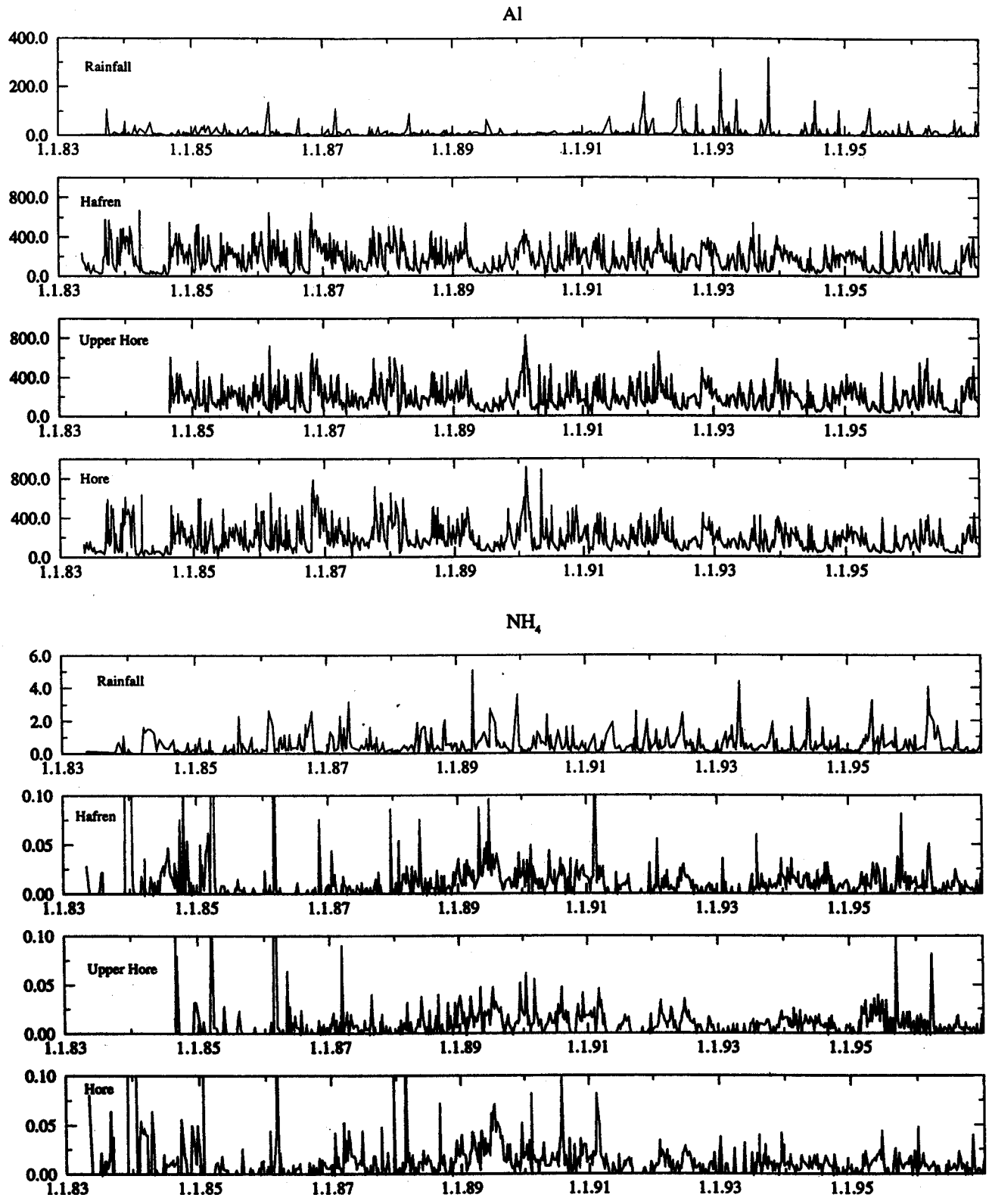
| | | min | max | baseflow | stormflow | avg | flow avg |
|---|---|---|---|---|---|---|---|
| Be | µg/l | 0.00 | 0.27 | 0.02 | 0.09 | 0.06 | 0.08 |
| Br | µg/l | 12.00 | 62.00 | 24.59 | 21.73 | 21.62 | 21.46 |
| Co | µg/l | 0.17 | 3.17 | 0.68 | 1.49 | 1.49 | 1.57 |
| Cr | µg/l | 0.00 | 49.31 | 2.90 | 2.00 | 1.90 | 1.96 |
| Cu | µg/l | 0.61 | 24.70 | 1.86 | 2.87 | 2.12 | 2.59 |
| Fe | µg/l | 30.70 | 289.10 | 118.72 | 95.99 | 83.99 | 88.20 |
| I | µg/l | 0.40 | 3.40 | 1.07 | 1.16 | 0.94 | 1.04 |
| Li | µg/l | 0.55 | 3.53 | 1.83 | 1.68 | 2.01 | 1.81 |
| Mn | µg/l | 5.95 | 51.25 | 15.27 | 19.01 | 21.16 | 20.33 |
| Ni | µg/l | 0.17 | 16.04 | 1.54 | 1.81 | 1.71 | 1.82 |
| Pb | µg/l | 0.00 | 31.24 | 2.58 | 13.43 | 6.23 | 10.79 |
| Sr | µg/l | 1.20 | 8.66 | 6.13 | 3.70 | 4.85 | 4.15 |
| Y | µg/l | 0.06 | 0.57 | 0.11 | 0.35 | 0.23 | 0.31 |
| Zn | µg/l | 4.04 | 77.16 | 9.11 | 16.58 | 14.03 | 16.00 |
| pH | | 4.32 | 7.66 | 7.18 | 4.62 | 5.97 | 5.10 |
| $Alk_{Gran}$ | µeq/l | –53.04 | 253.76 | 159.41 | –28.12 | 36.61 | –7.81 |

*Appendix Table 5.* Major, minor and trace element summary for Afon Hore water for felling years (1986–1991).

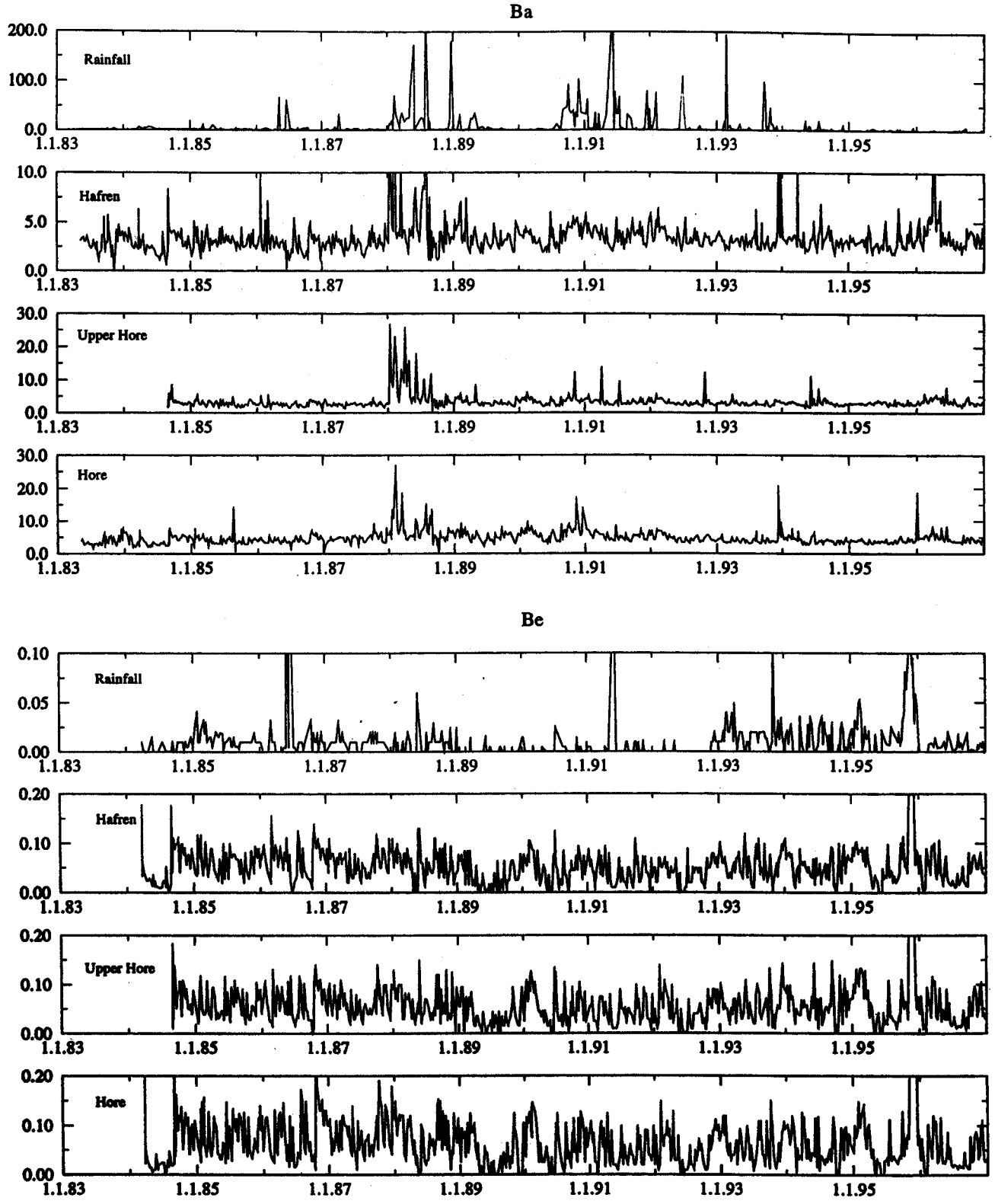
| | | min | max | baseflow | stormflow | avg | flow avg |
|---|---|---|---|---|---|---|---|
| Na | mg/l | 2.12 | 8.71 | 4.22 | 4.26 | 4.24 | 4.10 |
| K | mg/l | 0.10 | 0.70 | 0.18 | 0.31 | 0.22 | 0.30 |
| Ca | mg/l | 0.55 | 3.95 | 2.86 | 0.89 | 1.68 | 1.12 |
| Mg | mg/l | 0.40 | 1.42 | 1.10 | 0.78 | 0.93 | 0.81 |
| $NH_4$ | mg/l | 0.00 | 0.20 | 0.02 | 0.02 | 0.02 | 0.02 |
| Cl | mg/l | 4.70 | 21.80 | 7.57 | 8.32 | 7.89 | 7.76 |
| $SO_4$ | mg/l | 2.69 | 10.92 | 4.79 | 4.56 | 4.74 | 4.70 |
| $NO_3$ | mg/l | 0.40 | 4.70 | 1.33 | 2.80 | 2.40 | 2.69 |
| $PO_4$ | mg/l | 0.00 | 0.17 | 0.06 | 0.02 | 0.03 | 0.02 |
| F | mg/l | 0.00 | 0.21 | 0.05 | 0.06 | 0.06 | 0.06 |
| DOC | mg/l | 0.00 | 3.90 | 0.98 | 1.84 | 1.25 | 1.65 |
| Si | mg/l | 0.00 | 2.35 | 1.83 | 0.99 | 1.46 | 1.13 |
| Al | µg/l | 12.00 | 919.50 | 92.71 | 539.46 | 240.16 | 427.52 |
| B | µg/l | 2.50 | 66.50 | 6.69 | 4.96 | 5.92 | 5.35 |
| Ba | µg/l | 0.01 | 27.05 | 3.88 | 7.00 | 5.70 | 6.38 |
| Be | µg/l | 0.00 | 0.20 | 0.02 | 0.13 | 0.07 | 0.11 |
| Br | µg/l | 10.00 | 80.00 | 25.98 | 25.63 | 24.77 | 24.27 |
| Co | µg/l | 0.07 | 4.55 | 0.97 | 2.43 | 2.18 | 2.42 |
| Cr | µg/l | 0.00 | 39.60 | 4.60 | 4.42 | 3.76 | 3.73 |
| Cu | µg/l | 0.71 | 15.80 | 2.14 | 3.37 | 2.15 | 2.90 |
| Fe | µg/l | 5.70 | 412.60 | 79.93 | 88.36 | 66.48 | 88.17 |
| I | µg/l | 0.50 | 1.90 | 1.08 | 1.11 | 0.97 | 1.04 |
| Li | µg/l | 0.08 | 4.71 | 1.99 | 2.08 | 2.40 | 2.17 |
| Mn | µg/l | 14.92 | 86.65 | 26.54 | 39.62 | 37.17 | 39.72 |
| Ni | µg/l | 0.44 | 20.09 | 1.75 | 2.89 | 2.59 | 2.79 |
| Pb | µg/l | 0.00 | 20.02 | 2.73 | 9.41 | 4.65 | 7.72 |
| Sr | µg/l | 2.40 | 10.00 | 7.56 | 5.06 | 6.25 | 5.39 |
| Y | µg/l | 0.01 | 0.55 | 0.12 | 0.33 | 0.23 | 0.30 |
| Zn | µg/l | 2.30 | 43.10 | 8.29 | 26.26 | 20.18 | 25.24 |
| pH | | 4.39 | 7.55 | 7.00 | 4.67 | 5.78 | 5.00 |
| $Alk_{Gran}$ | µeq/l | –46.63 | 428.67 | 110.07 | –22.57 | 22.85 | –10.33 |



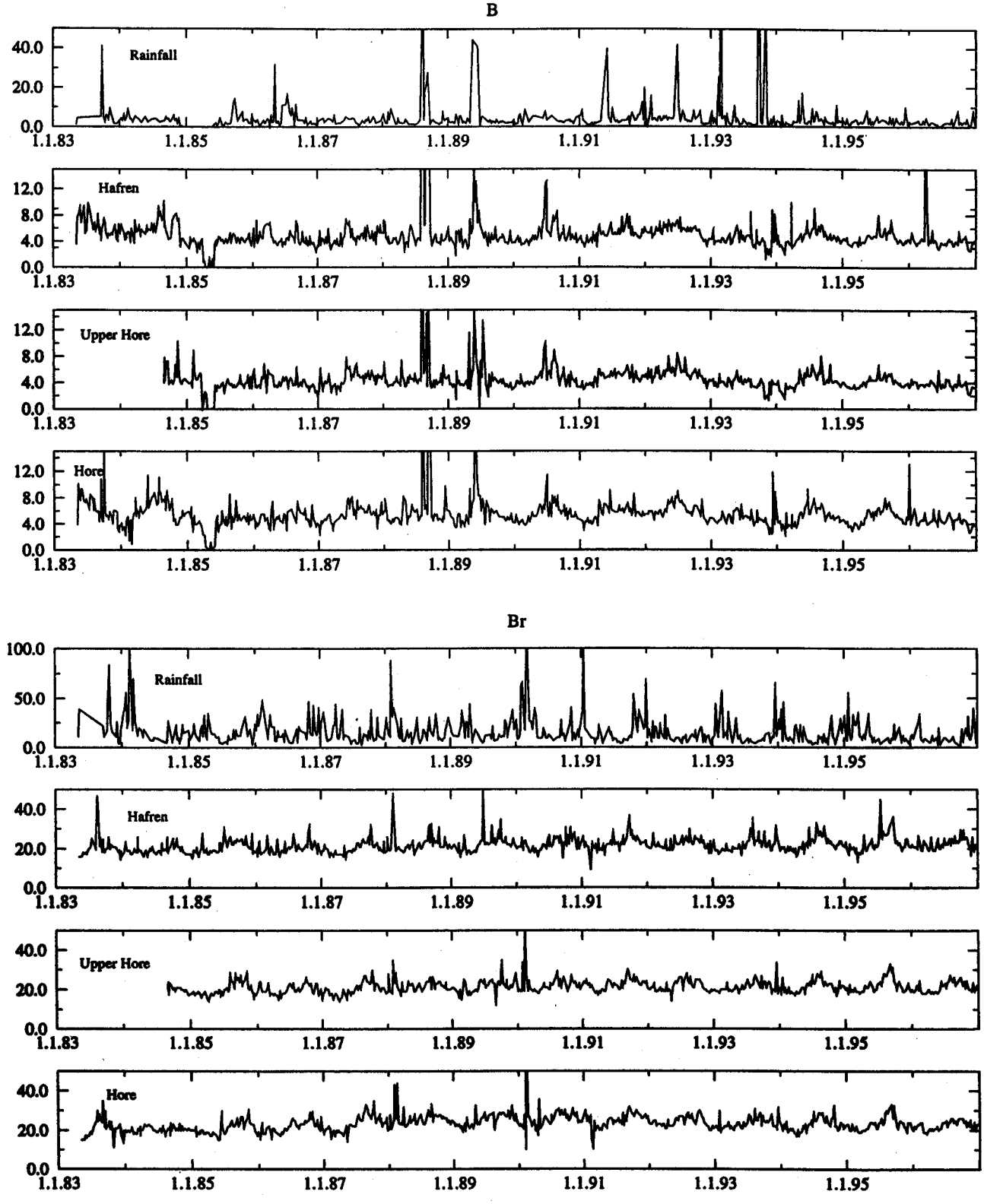

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for alkolimity (Alk–low: μEq/l) and pH.*



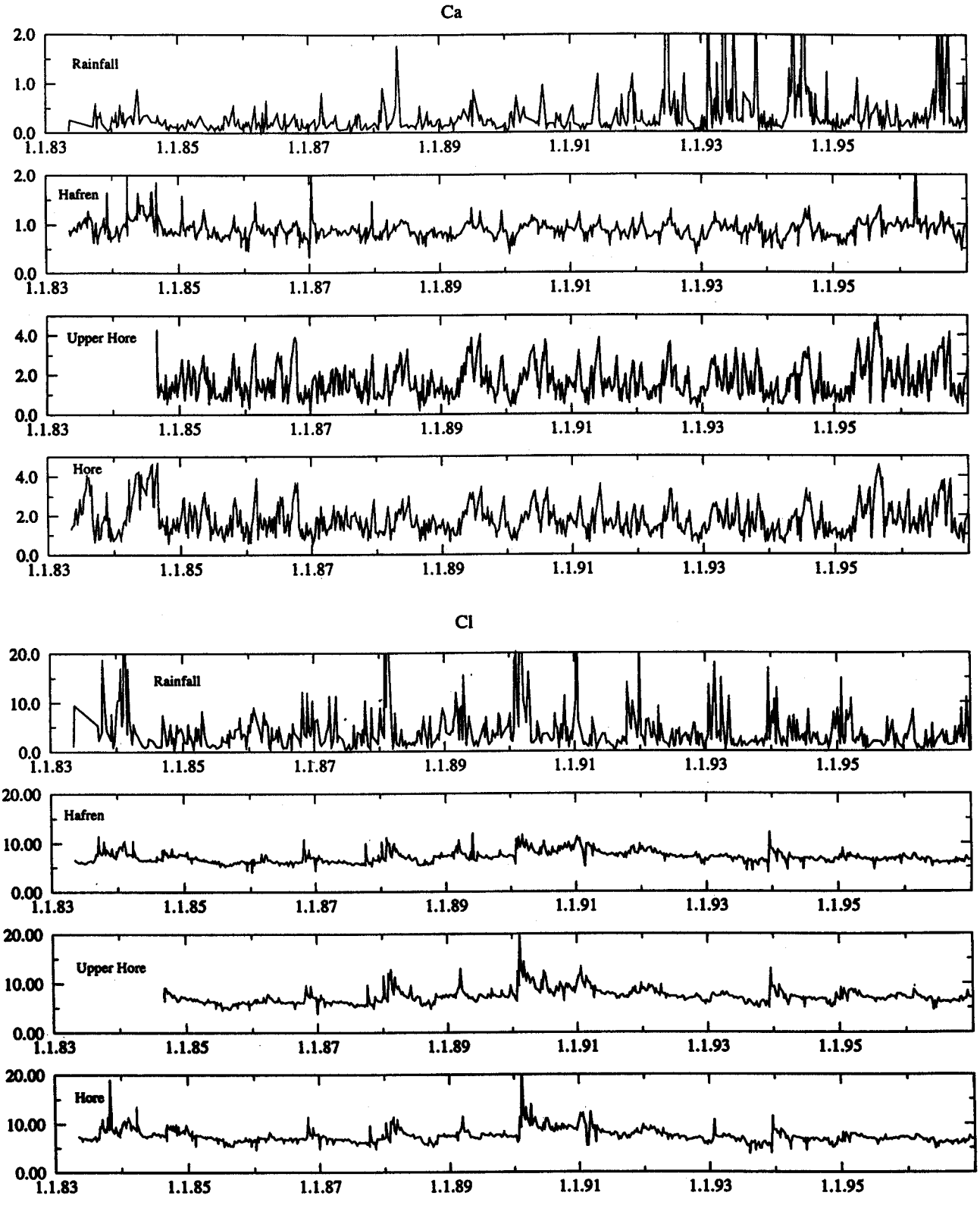

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for aluminium (µg/l) and ammonium (mg-$NH_4$/l).*



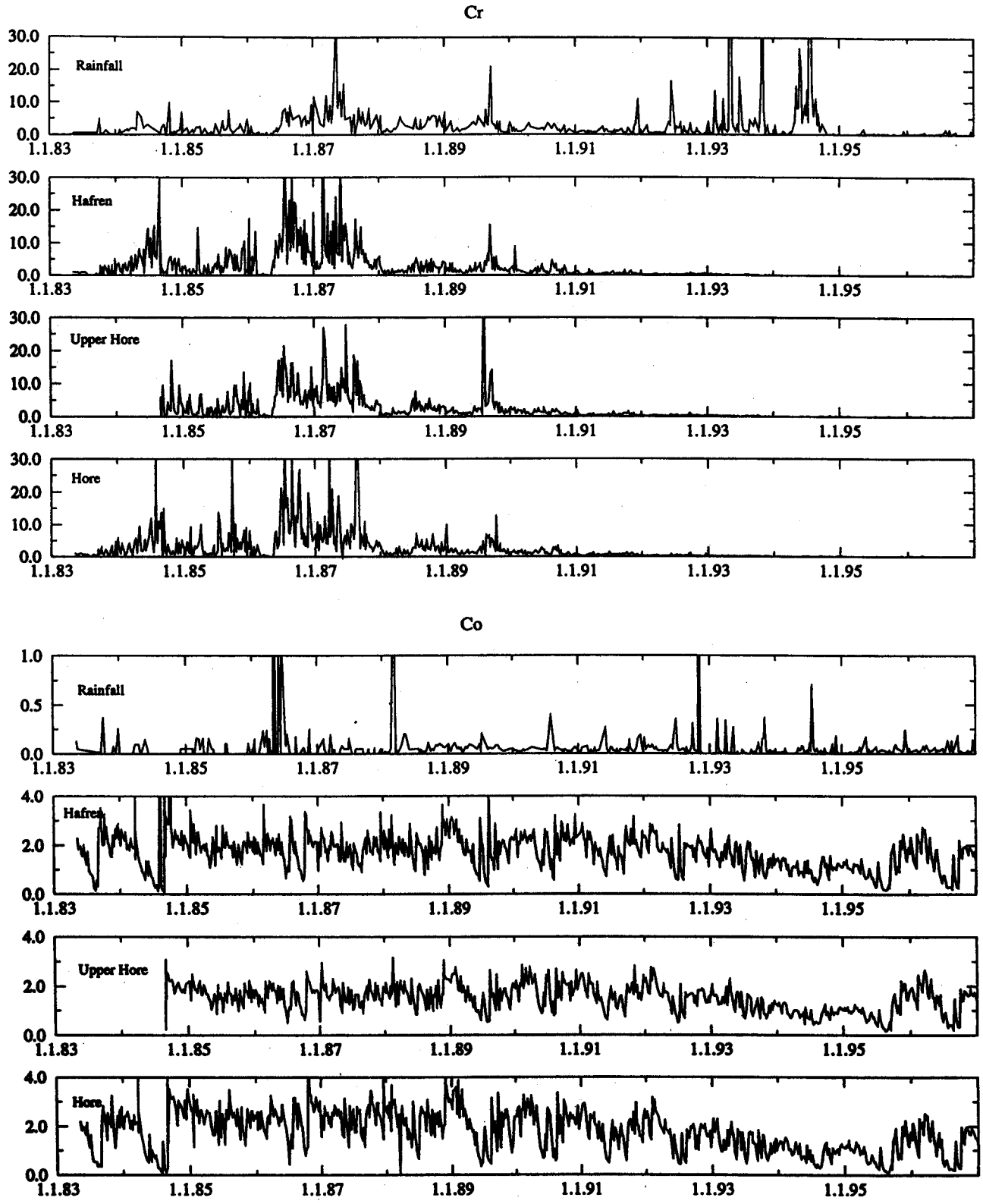

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for barium (μg/l) and beryllium (μg/l).*



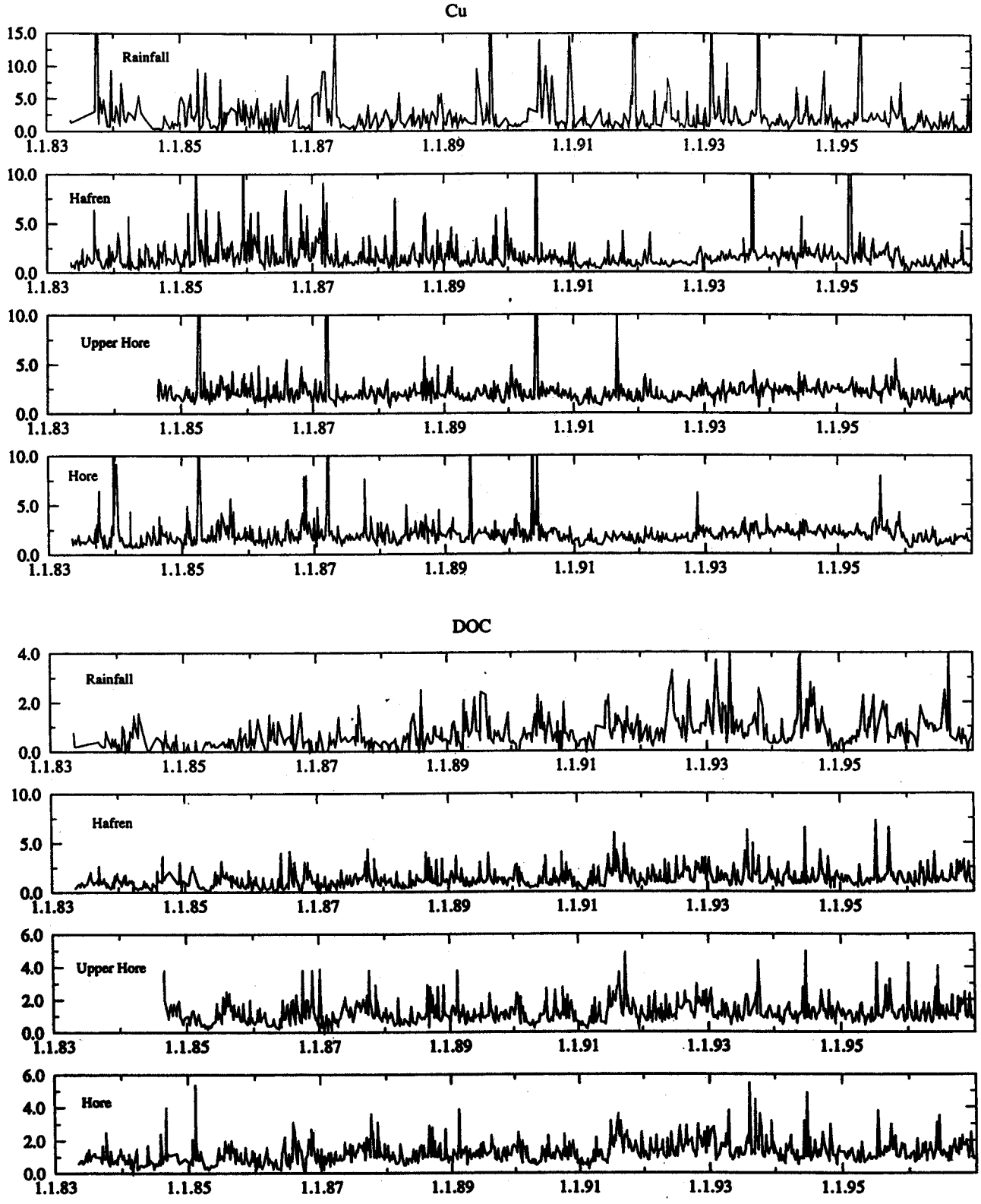

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for boron (μg/l) and bromide (μg/l).*



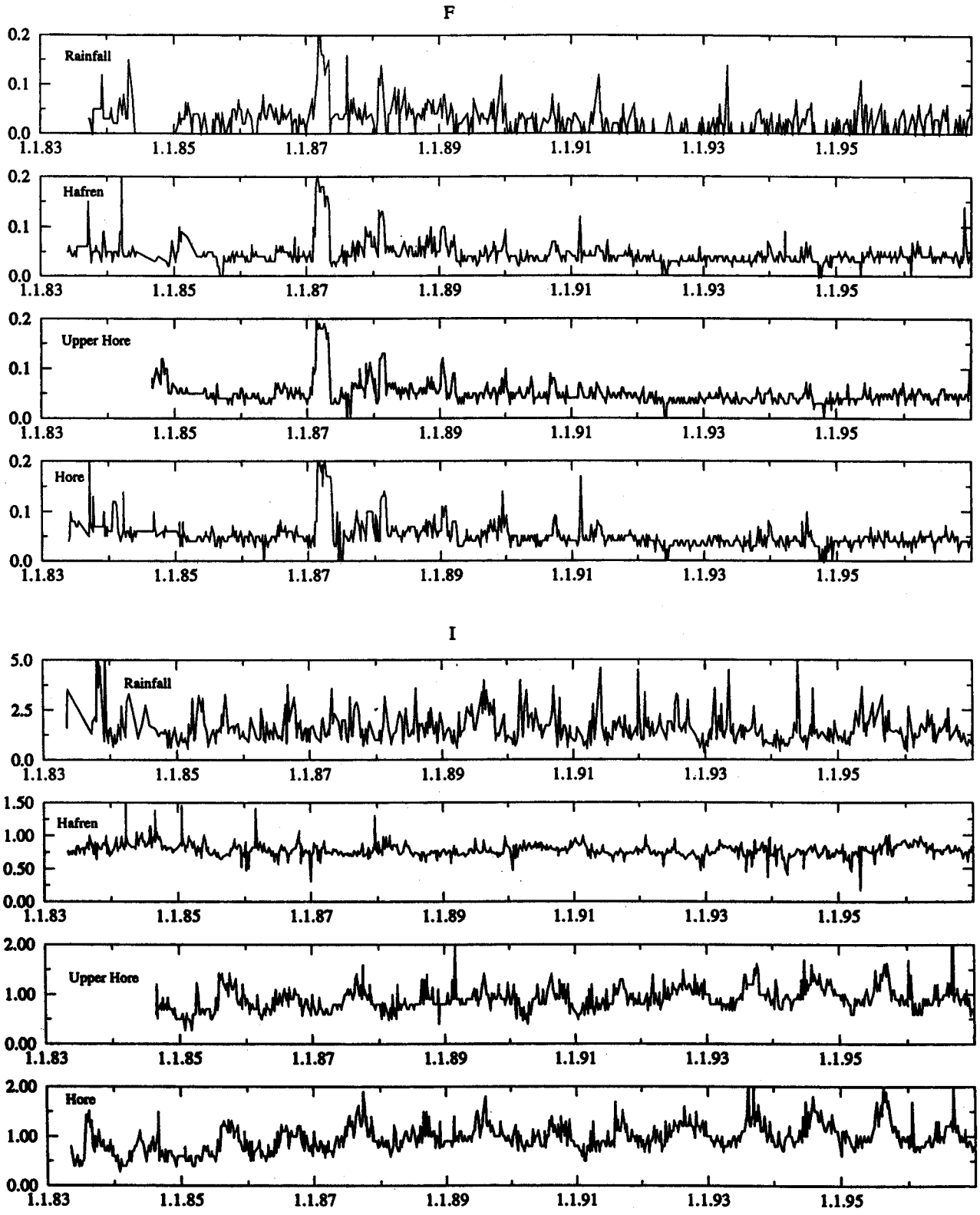

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for calcium (mg/l) and chloride (mg/l).*



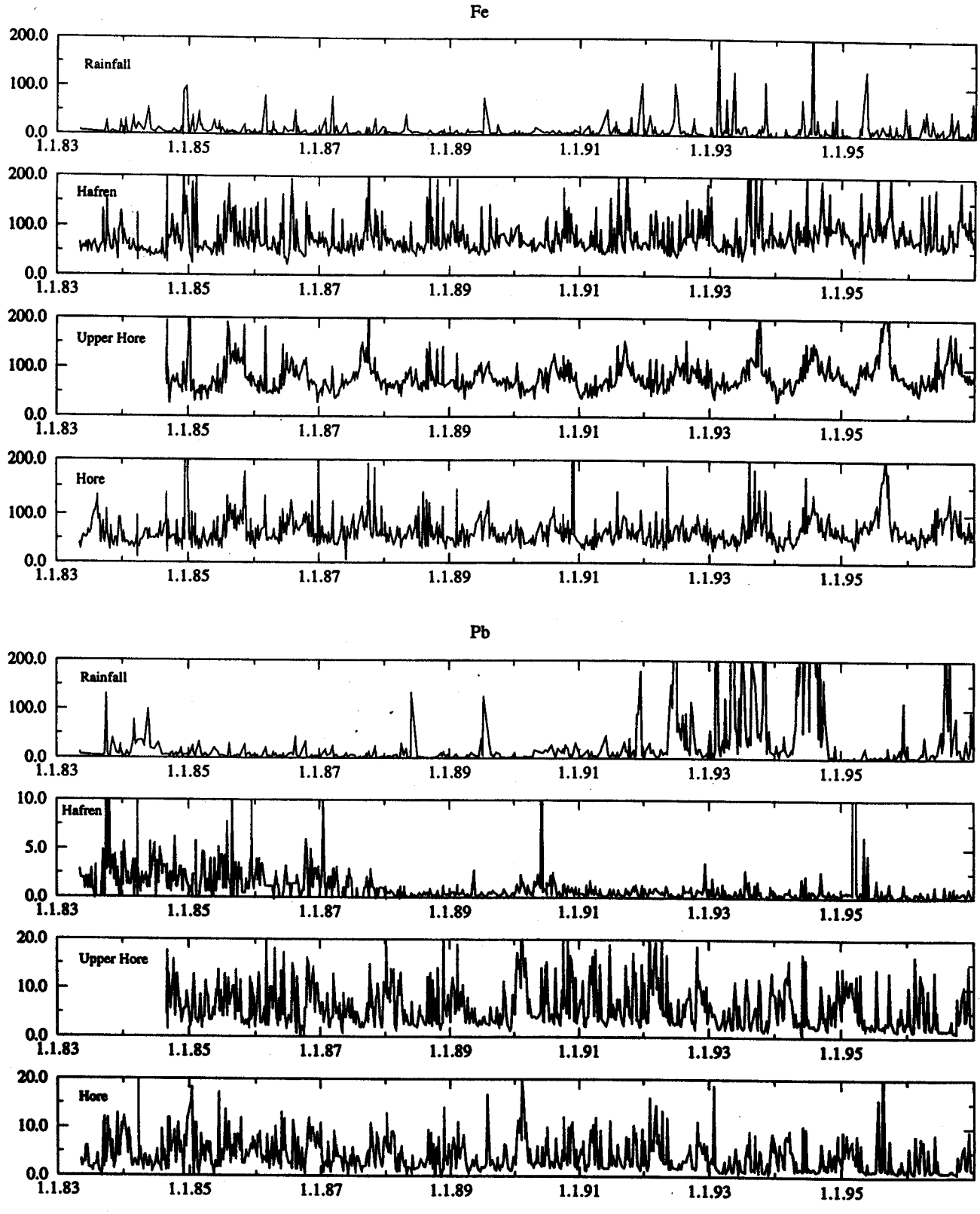

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for chromium (μg/l) and cobalt (μg/l).*



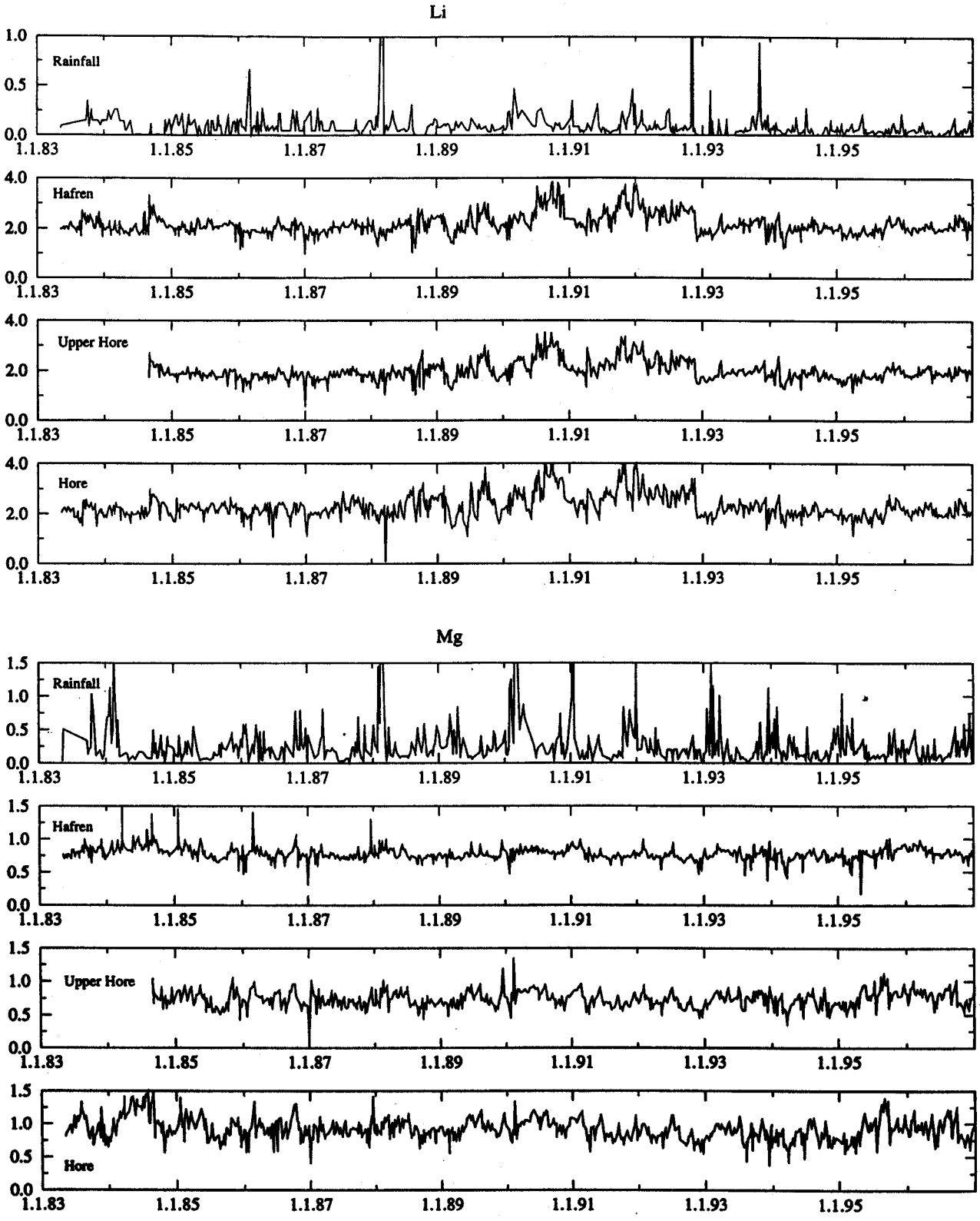

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for copper (μg/l) and dissolved organic carbon (mg-C/l).*



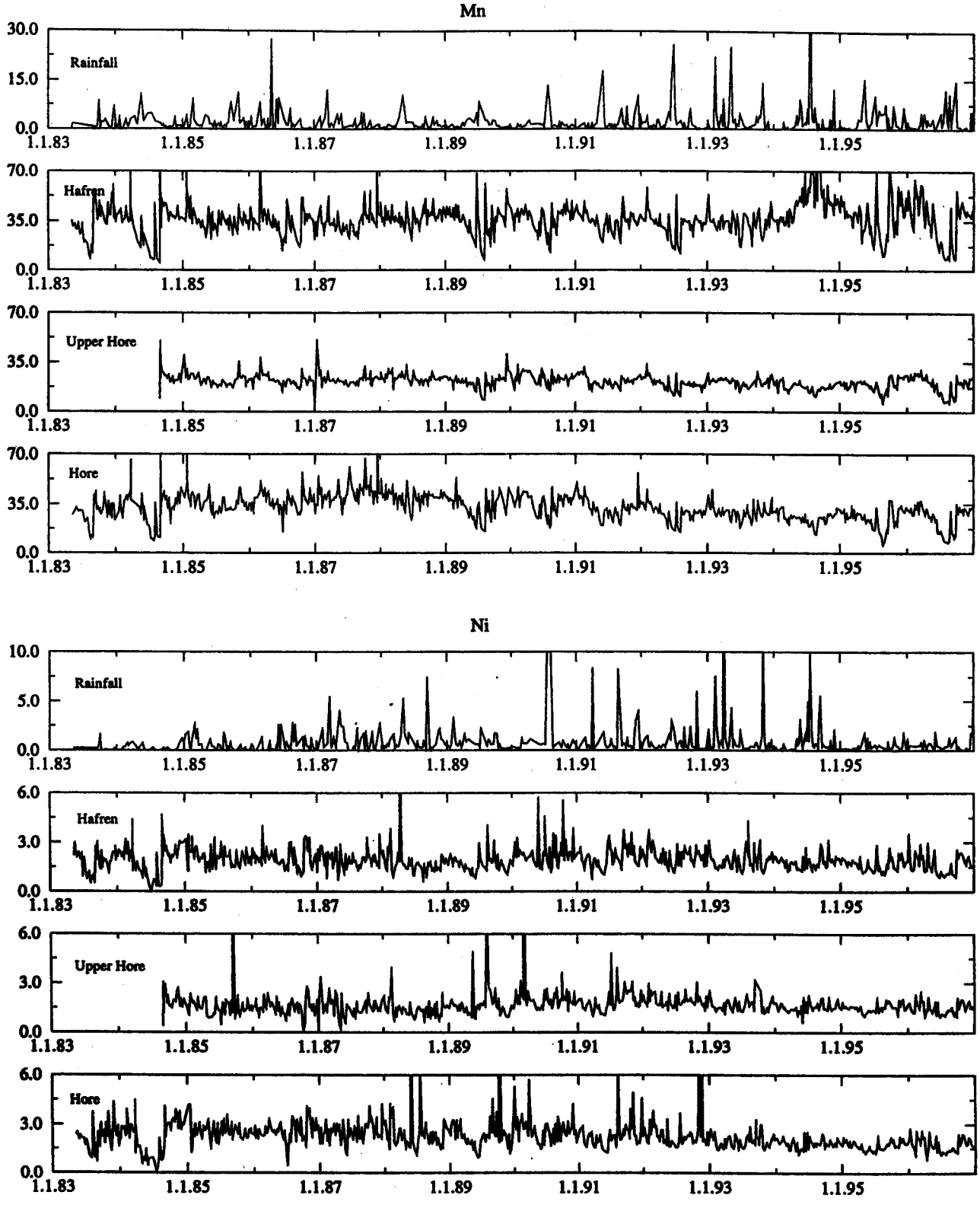

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for total fluorine (mg/l) and total iodine (μg/l).*



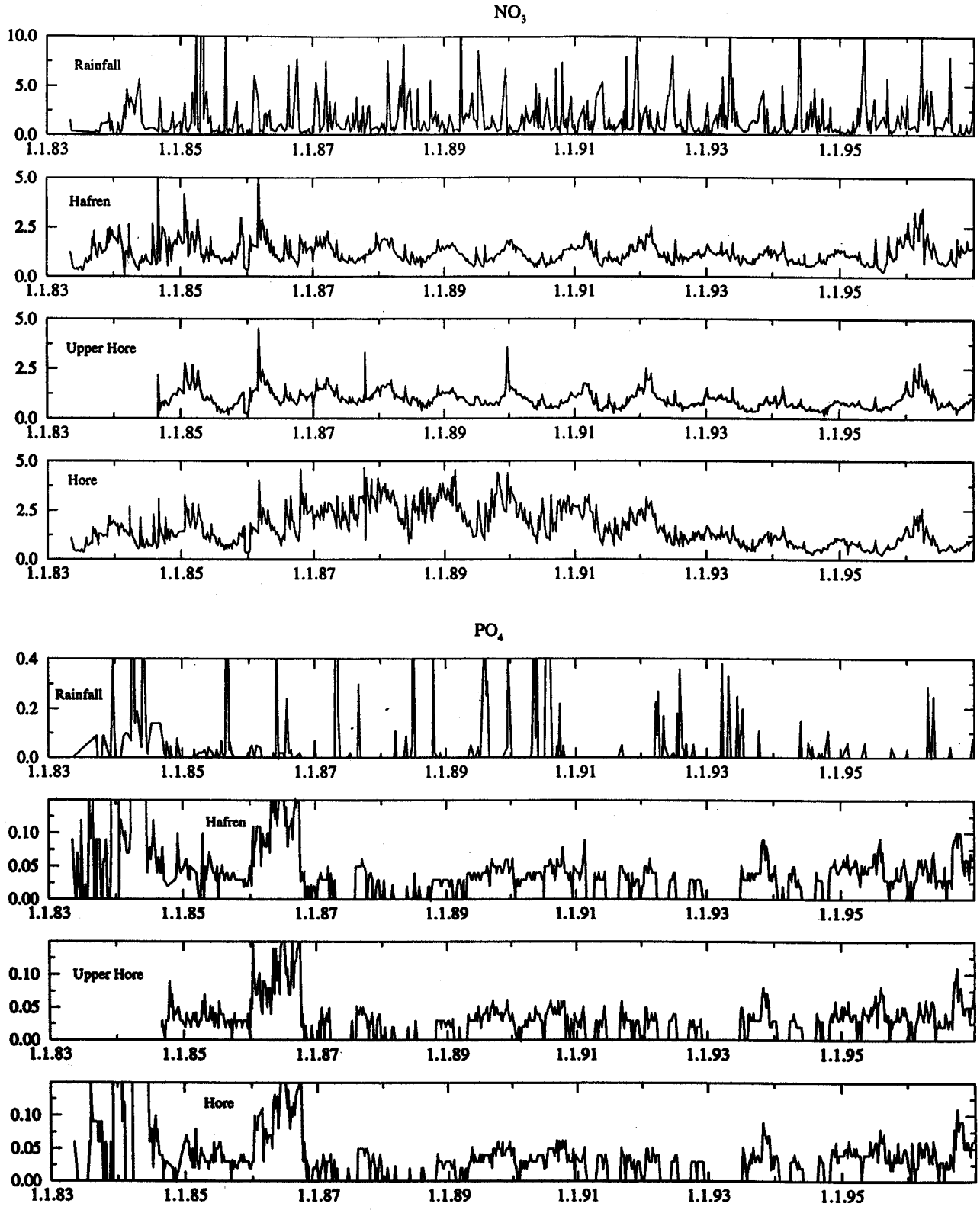

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for iron (μg/l) and lead (μg/l).*



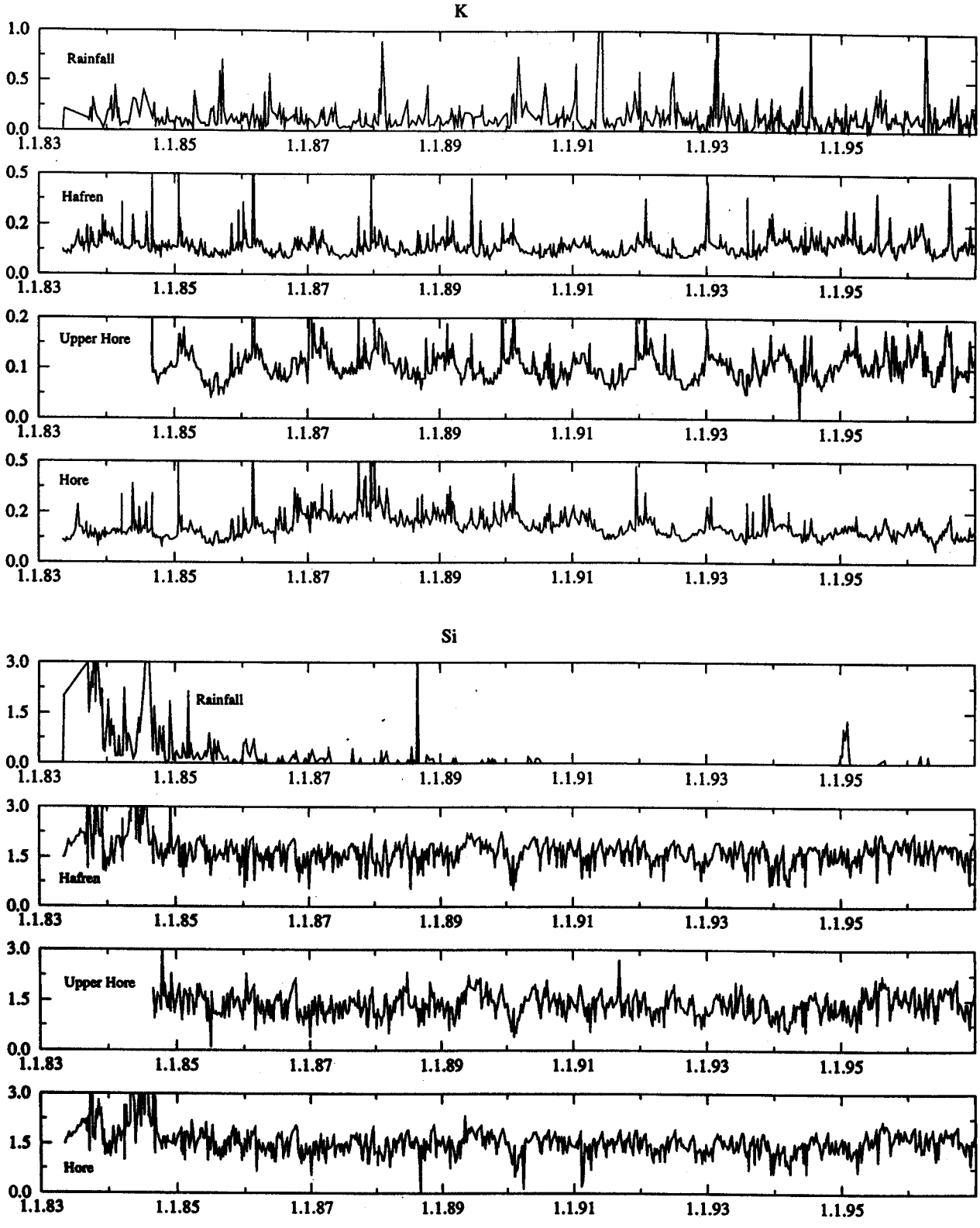

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for lithium (μg/l) and magnesium (mg/l).*



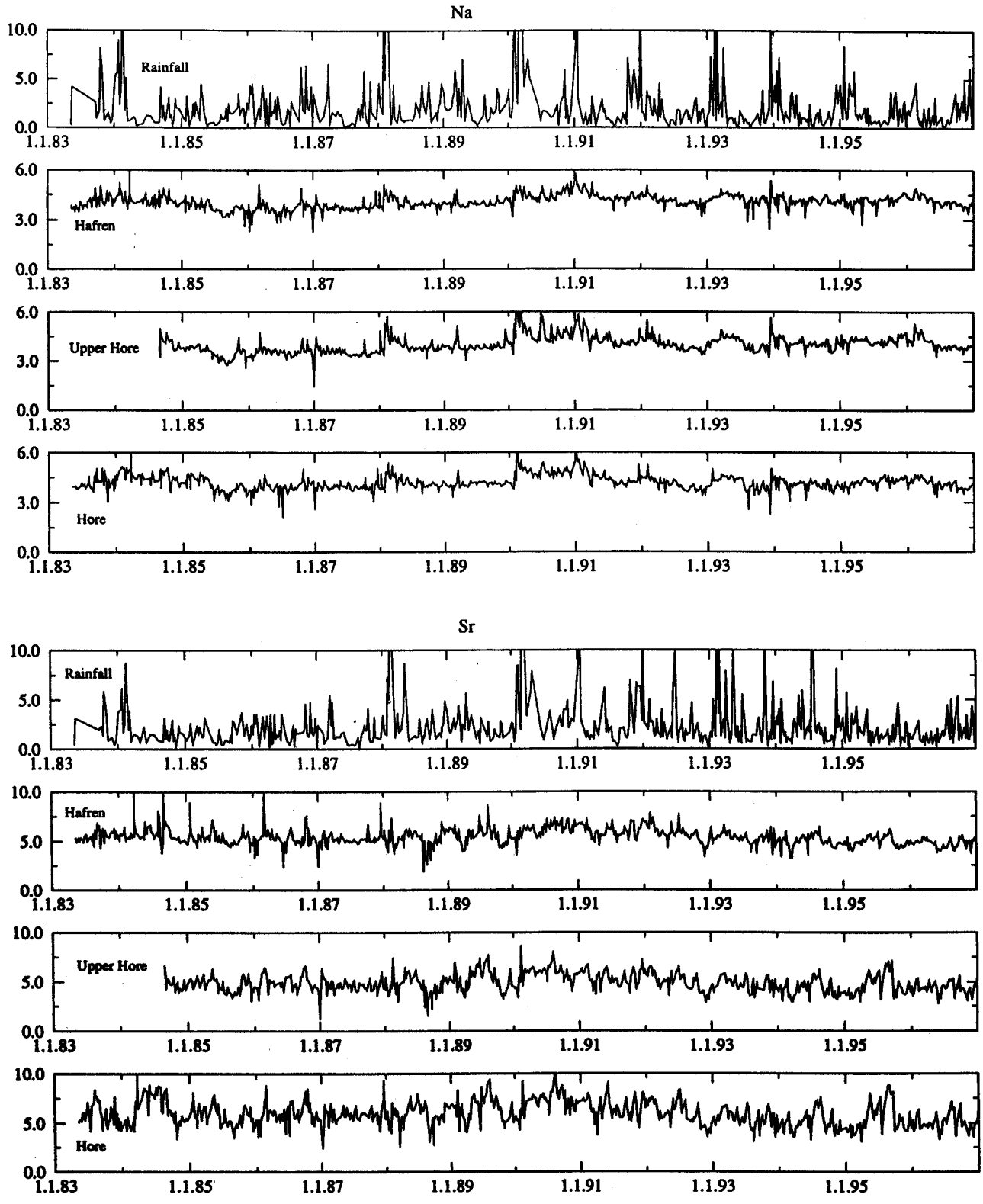

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for manganese (μg/l) and nickel (μg/l).*



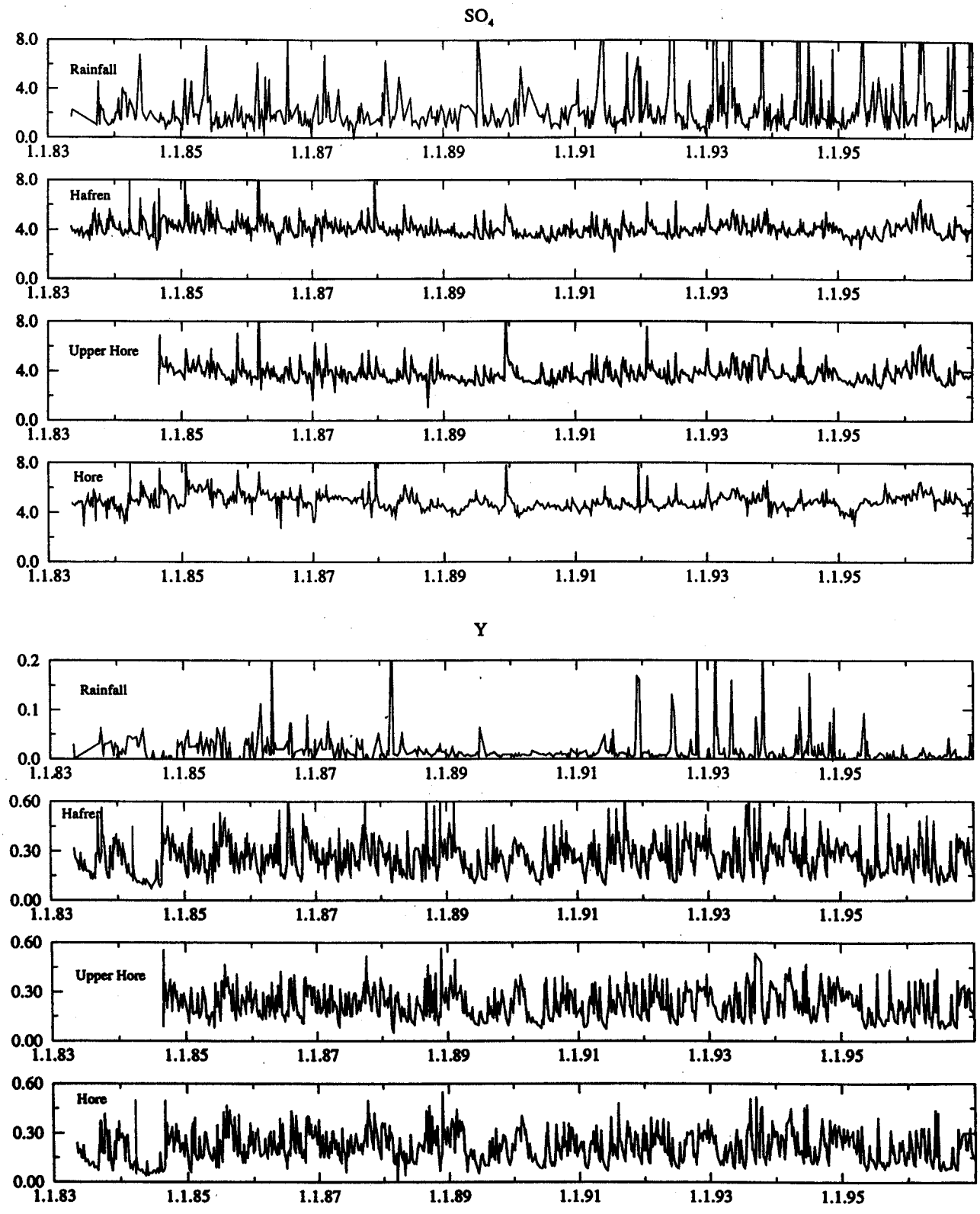

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for nitrate (mg-$NO_3$/l) and phosphate (mg-$PO_4$/l).*



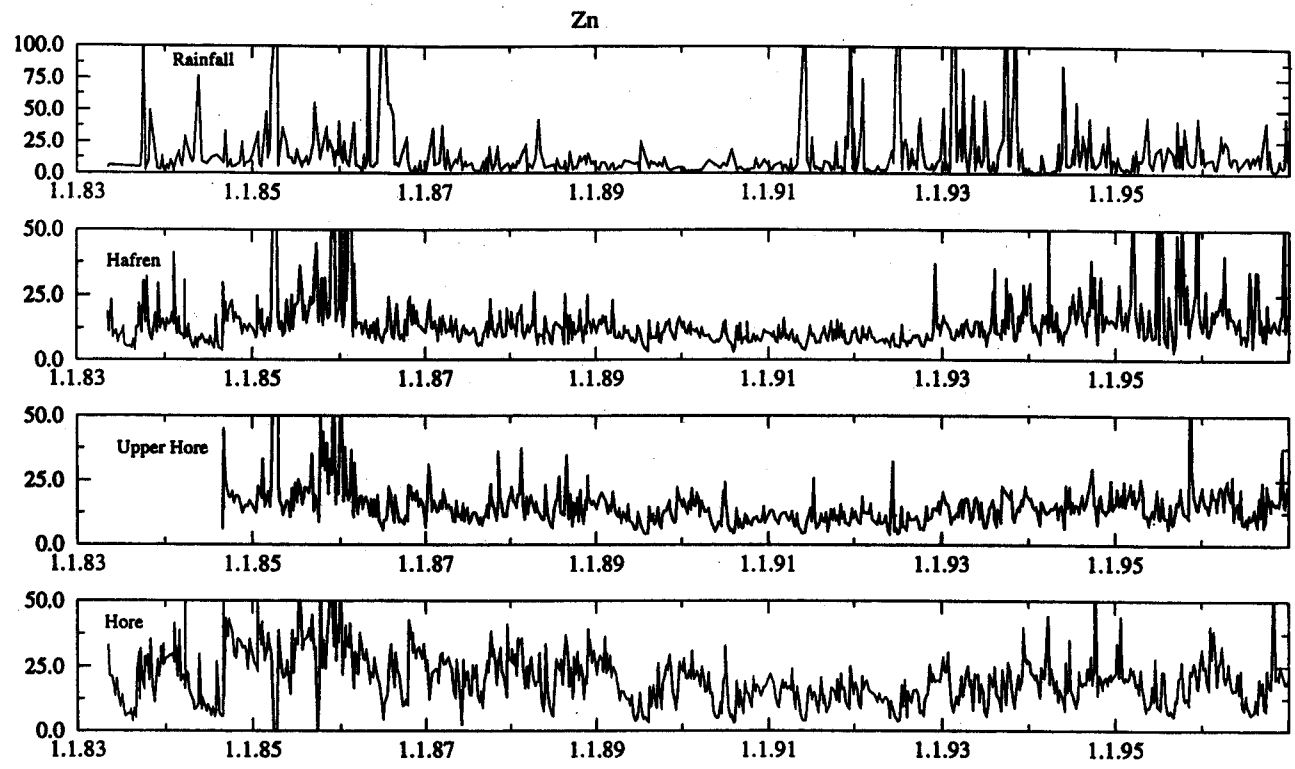

Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for potassium (mg/l) and silicon (mg/l).*




Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for sodium (mg/l) and strontium (μg/l).*




Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for sulphate (mg-$SO_4$/l) and yttrium (μg/l).*




Appendix Fig. 1. *Time series for rainfall, Afon Hafren, Afon Hore and upper Afon Hore waters for zinc (μg/l).*